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THE AMERICAN CERAMIC SOCIETY

Vol. 26 May 1, 1943 No. 5

STUDY OF PHOTOLUMINESCENCE IN GLASS*

By A. R. Rodriguez, C. W. Parmelee, and A. E. Badger

Abstract

The influence of composition and temperature on the fluorescence of glasses containing uranium and glasses containing cuprous oxide and stannous oxide was investigated. Secondary cations reduce the fluorescence of uranium in the glasses studied, depending to a certain extent on the electrostatic conditions they produce in the glass structure. The intensity of fluorescence as well as the structure of the spectrum diminishes in the order of phosphate, silicate, and borate glasses of equivalent compositions, which shows that fluorescence is favored by increase of oxygen in the glass structure without increasing the interfering secondary cations. Raising the temperature greatly diminishes the intensity of the fluorescence as well as the structure of the spectrum of glasses containing uranium. The fluorescence of the glasses containing cuprous oxide and stannous oxide as activators seems to be favored by increase in lime and increase in silica. These glasses possess appreciable phosphorescence, which appears to be enhanced by increase in silica and decrease in lime. A peculiar property of this type of luminescent glass is a maximum which it exhibits in its fluorescence-temperature relationship. There are indications that electrons are set free from the excited centers (copper atoms or small groups of copper atoms), which wander about in the glass structure.

I. Introduction

The study of fluorescence in glass is interesting both from the theoretical and the practical points of view. The phenomenon of fluorescence is significant theoretically in that it represents an inner expression of the atoms and molecules and therefore can give information on their structure and behavior. The fluorescing center is influenced to a certain extent by its neighbors, and fluorescence is therefore an excellent method for investigating the hyperfine structure of matter. Some fine structures revealed by fluorescence spectra cannot be detected by the excellent method of X-ray diffraction.

The introduction of modern fluorescent lighting is the outcome and the cause of the intensive study of the fluorescence of solids in general. This technique may be used to give information relating to the presence or absence of certain elements in glass.[1] It may also be applied in the detection of strain and cords in glasses.[2] A recent use of fluorescent glasses is in the viewing screens of television tubes.[3]

The more efficient fluorescence of crystalline substances as compared to glasses has led to a comparative neglect of the study of fluorescence in the latter.

(1) Some General Considerations

Light totally absorbed by matter (1) may be re-emitted with the same wave length; (2) only part of the absorbed light energy may be re-emitted at a longer wave length, and the remainder is converted into some other form of energy, such as heat; (3) no radiation at all may be given off, all the energy being converted into heat; or (4) it may be used up in a photochemical reaction or ionization.

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This investigation was submitted by the senior author in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering, Graduate School, University of Illinois, Urbana, Ill.

[1] (a) P. Gilard, L. Dubrul, and D. Crespin, "Fluorescence du Verre," *Verre & Silicates Ind.*, 9 [22] 253–57; [23] 266–70 (1938); *Ceram. Abs.* 18 [2] 46 (1939).

(b) P. Gilard, L. Dubrul, F. Jamar, and D. Crespin, "Fluorescence of Glass," *Verre & Silicates Ind.*, 8 [35] 414–16 (1937); *Ceram. Abs.*, 17 [7] 247 (1938).

(c) W. R. Lester, "Fluorescence of Certain Colored Glasses," *Glass Ind.*, 12 [4] 83 (1931); *Ceram. Abs.*, 10 [6] 416 (1931).

[2] M. A. Besborodov and N. O. Abelchuk, "Note on Use of Fluorescence Tests for Identification of Striae and Cords," *Jour. Soc. Glass Tech.*, 23, 73–75 (1939); *Ceram. Abs.*, 18 [9] 241 (1939).

[3] M. Curie, "Phosphorescent Glasses, Decay of Phosphorescence," *Trans. Faraday Soc.*, 35, 114 (1939).

The first condition is termed "resonance radiation" and occurs chiefly in extremely rarefied monatomic gases. Under this condition, the atoms of the gas are very far apart and can emit radiation with little or no disturbance from their neighbors. This may well be exemplified by the gases of mercury and sodium, which have been the subject of extensive investigation by Wood* and his co-workers.

If the pressure of these rarefied gases were increased, the resonance fluorescence would be modified, and light with a longer wave length than the exciting light would be emitted. The emitting center, or atom, collides with its neighbors, inasmuch as they are nearer under these conditions. Some of the absorbed light energy is transferred into kinetic energy, thus leaving the emitted radiation with a lower energy and therefore a longer wave length. This latter phenomenon is termed "fluorescence." That the fluorescent light is usually of longer wave length than the exciting radiation was made known long ago by Stokes. Anti-Stokes fluorescence, namely, fluorescence of shorter wave length than that of the exciting light, may take place, however, under special conditions. Resonance radiation does not usually occur in solids and liquids because, in those states, the atoms and molecules have a strong influence on each other.

When fluorescence continues for some time after the exciting source has been removed, the phenomenon is termed "phosphorescence." There have been recent attempts to make a fundamental distinction between the terms "phosphorescence" and "fluorescence." Pringsheim[4] states that phosphorescence would consist of an emission process in which the fluorescing center goes from a metastable to a ground state. This definition is an attempt to remove the arbitrary distinction of length of time in order to distinguish the two processes and to identify them in relation to their emission mechanisms. This idea encounters some difficulties and has not yet met with general acceptance. Some writers refer to phosphorescence as the afterglow which lasts longer than 10^{-6} seconds.

(2) Concerning Spectra

The origin of the spectra was not satisfactorily explained until 1913, when Bohr introduced the idea of "stationary states" or energy levels in which the energy of an isolated atom does not vary continuously but varies in steps characteristic of each stationary state. Radiation is emitted when an atom changes from one energy level to another. This corresponds to a transition of an electron from an outer orbit of higher energy level to an orbit of lower energy level. Absorption is the reverse process, namely, a transition from an inner orbit to an outer one. The frequency of the radiation is given by equation (1).

$$\nu = \frac{E_1 - E_0}{h} \qquad (1)$$

E_0 = energy of initial quantum state.
E_1 = final state.
h = Planck constant.

This idea of energy levels is applicable not only to atoms but also to molecules and crystals in general. The idea of the circular orbits of Bohr has been modified by Sommerfeld to include elliptical and hyperbolic orbits as well to account for the multiplicity of the lines. The newer concept of wave mechanics renounces all of these atomic models and describes the atom by means of mathematical equations.

Just as definite energy states exist in atoms as a result of electron configuration, such discrete energy states also exist in molecules. The situation, however, is more complicated as it contains rotational and vibrational energies, in addition to electronic energy, so that the Bohr frequency, $\nu = E/h$, would take the form of equation (2).

$$\nu = \frac{E_e + E_r + E_v}{h} \qquad (2)$$

Where E_e, E_r, and E_v = electronic, rotational, and vibrational energies, respectively.

Changes in the rotational energy are small so that pure rotation spectra occur in the infrared region. A pure vibrational spectrum is often coupled with a rotational spectrum giving a rotation-vibration spectrum which likewise makes its appearance in the long wavelength region. Spectra resulting from changes in electronic energy occur in the visible and ultraviolet portions of the spectrum. Changes in pure electronic energy ($\nu = E_e/h$) are manifest as distinct discrete lines, whereas simultaneous changes in electronic, rotational, and vibrational energy bring about electronic bands in the visible and ultraviolet portions of the spectrum. The bands seem to be continuous, but each of them really consists of a group of discrete lines very close together. These separations may be seen only with an instrument of high dispersive power. Because changes in rotational or vibrational energy are small, the lines come very close together, giving the appearance of a continuous spectrum.

In addition to these discrete spectra that may appear as well-separated lines and as electronic bands, which in reality are discrete lines very close together, there is another type of spectrum, namely, the continuous spectrum, which cannot be separated into lines. This means that the atom or molecule assumes a continuous series of energy states. According to the quantum theory, such continuous possibilities can exist only when nonperiodic processes take place, whereas only discrete energy levels occur in periodic processes. In isolated atoms, this happens when a transition occurs between an elliptic orbit (periodic) and a hyperbolic orbit (nonperiodic). In this process, the electron that has jumped from an elliptic to a hyperbolic orbit continuously recedes from the nucleus and finally separates itself from the latter, which is the process constituting an ionization. Part of the absorbed energy is used up as ionization energy, which would produce a continuous absorption spectrum. Emission occurs when the reverse process takes place. In isolated molecules, a continuous absorption spectrum is indicative of dissociation into atoms.

Continuous spectra occur chiefly in condensed sys-

* See general reference No. 8, p. 150.

[4] P. Pringsheim, "General Discussion on Luminescence," *Trans. Faraday Soc.*, **35**, 87 (1939).

tems, liquid and solid, where the atoms or molecules are so close together that collisions are possible as well as an interaction of their magnetic and electric fields. In this state, the discrete energy states of the isolated atom will be modified by the disturbance of the neighboring atoms, giving the spectrum a certain width.

Substances in liquid solution usually fluoresce much less and with bands more diffuse than those in solid solution, which is the result of the greater disturbance by the solvent molecules in the liquid state. Concentrated solutions, moreover, often fluoresce less than dilute solutions. It is this continuous nature of the spectra of solids and solutions that makes their interpretation difficult because no definite transitions can be attached to them.

In the rare earths, the alteration of the spectra caused by outside disturbances is relatively small owing to the fact that the electrons responsible for the emission are in the 4f shell, which is shielded by the outer electrons. Similar shielding exists in the fluorescence of the uranyl salts where the seat of emission is ascribed to the coordination group UO_2^{++}. For atoms, the fluorescence of which is caused by the outermost or valence electrons, the nature of the spectra, of course, would be greatly influenced by their neighbors.

A pure crystalline solid usually does not fluoresce, but it exhibits photoluminescence when definite amounts of impurities of heavy metals are incorporated with it. This photoluminescence is ascribed to distortions set up in the lattice by the impurity atom. Another cause of lattice distortion is found in the formation of "defect structure," which is exemplified by zinc oxide and the tungstates. When zinc oxide is heated, it gives off oxygen atoms leaving those positions vacant.

The classic works of Bequerel and Lenard and coworkers on crystal phosphors are well known, and greater effort is being directed at the present time toward work on the fluorescence of crystalline solids.

Relatively little systematic study, however, has been done on the fluorescence of glasses. Glass, from recent studies of its structure, may be a unique state of matter very distinct from that of a solid or a liquid. It has both the rigidity of a solid and the disorderliness of a liquid. It may perhaps be termed a "confused crystal." For this reason, this state of matter opens an interesting field of investigation.

(3) Review of Literature

Schmidt[5] as early as 1896 worked on the fluorescence of uranium glass and observed an emission maximum at 5350 a.u. and an absorption maximum at 4970 a.u. Nichols and Merritt,[6] working on a similar glass with a spectrophotometer, found a maximum at 5340 a.u. They also discovered that fluorescence occurred as far as the wave length of 5390 a.u. in the exciting light, but the fluorescence spectra did not change with variation in wave length of the exciting light. Stokes' law, furthermore, was not fulfilled. Geiger[7] and Gibbs[8] determined the variation of fluorescence with temperature of a uranium glass, and they established the fact that the intensity of fluorescence decreases continuously as the temperature increases with a shift of the spectrum toward longer wave lengths.

Weyl[9] found a great difference between the absorption spectra of uranous salt solutions and those in glass. Uranous glasses do not fluoresce; and according to Weyl, the uranyl-uranate equilibrium is favorable to the uranyl in the presence of strong electronegative heteropolyacid.

Burke[10] was able to detect fluorescence absorption in uranium glass, which differed from the "excited" to the unexcited condition.

Jäckel[11] observed that glass containing cadmium sulfide neither fluoresced nor showed its characteristic absorption of violet light when it was not allowed to "strike."* He concluded that fluorescence is first brought about by the formation of colloidal particles; the wave length of the emitted light shifts toward longer wave lengths as the particles become larger.

Eckert and Schmidt[12] observed that the addition of 0.5% of arsenic trioxide to a glass containing cerium caused phosphorescence, whereas only fluorescence occurred when no arsenic trioxide was used. Maximum fluorescence was obtained at 0.64% of cerium oxide, and the presence of titanium oxide neutralized the fluorescence.

The effect of one activator on the other is not additive as shown by Cohn.[13] Thermoluminescence of zinc borate glass which contains a small amount of manganese is increased by small additions of cerium but is decreased by larger amounts.

Pringsheim and Schlivitch[14] determined the fluorescence and absorption spectra of praeseodymium and neodymium glasses. Their results showed that didymium and cerium give a much more intense emission than didymium alone.

Sodium silicate glasses, with 0.01% of copper, 0.01% of chromium, and 0.1% of manganese, showed no phos-

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[5] G. C. Schmidt, "Beitrage zur Kenntnis der Fluoreszenz," *Ann. Physik.*, **58**, 103 (1896).

[6] E. Nichols and E. Merritt, "Studies in Luminescence," Carnegie Inst. of Washington (Washington, D. C., 1912), p. 19.

[7] M. Geiger, Kayser's Handbuch der Spectroscopie, Vol. IV, p. 1029. S. Hirzel, Leipzig, 1908.

[8] R. C. Gibbs, "Effect of Temperature on Absorption and Fluorescence," *Phys. Rev.*, **26**, 361 (1909).

[9] W. A. Weyl and E. Thümen, "Konstitution und Farbe der Uran Gläser," *Sprechsaal*, **67** [7] 95–97 (1934); *Ceram. Abs.*, **13** [7] 174 (1934).

[10] J. B. Burke, "Note on Fluorescence and Absorption," *Proc. Roy. Soc. London*, **A76**, 165 (1905).

[11] G. Jäckel, "Über einige Neutzeitliche Absorptionsgläser," *Z. Tech. Phys.*, **7**, 301 (1926); *Glasindustrie*, **34**, 349 (1926); *Ceram. Abs.*, **6** [7] 277 (1927).

* Glasses of certain compositions form their color, which is due to the formation of colloidal particles, by heat-treatment; the phenomenon is known as "striking."

[12] F. Eckert and E. Schmidt, "Der Einfluss von Cer und Arsen auf des Photochemische Verhalten von Silikatgläsern," *Glastech. Ber.*, **10** [2] 80–85 (1932); *Ceram. Abs.*, **11** [5] 295 (1932).
See also *Sprechsaal*, **60**, 793 (1927).

[13] B. E. Cohn, "Thermoluminescence in Glasses Which Contain Two Activators," *Jour. Amer. Chem. Soc.*, **52**, 5146 (1930).

[14] P. Pringsheim and S. Schlivitch, "Über die Fluoreszenz von Praesodymium und Neodymium Glas," *Z. Physik*, **61**, 297 (1930).

phorescence with ultraviolet light, but they exhibited this phenomenon with cathode rays (Schloemer[15]).

Lester[1(e)] distinguished glasses by their fluorescent color.

In his study of manganese and zinc silicate glasses, Dobischek[16] concluded that fluorescence occurs when zinc and manganese silicates are used.

Light of all absorption bands of the rare earths excited fluorescence as long as this was shorter than the luminescent wave length, according to Deutschbein[17] in his work on the rare earths. The spectra of the rare earths in glasses were found to be similar to those of their crystal phosphors except that the lines were wider. From a comparison of the emission spectra of europium in glass, water solution, and crystal, Tomaschek[18] derived some interesting conclusions on the structure of glass; glass, to him, is not a state between a solid and a liquid but a state unique in itself.

According to Wiehr,[19] phosphorescence does not appear except with crystallization.

Weyl[20] found that quenched silver glass showed little fluorescence. On reduction with hydrogen at about 150°C., these glasses showed a bright fluorescence which indicated that the silver atoms are probably the fluorescing centers; after further heating and reduction, the fluorescence shifted toward longer wave lengths.

Rexer[21] worked with sodium silicate of composition $Na_2Si_2O_5$, both in the glassy and crystallized condition, and found that crystallization favors phosphorescence. Like Wiehr,[19] he made phosphorescence a criterion for crystallinity. Curie,[3] working on zinc borate glass activated by manganese, also found that crystallization greatly increased phosphorescence.

The most extensive work on fluorescent glasses was published by Gilard, Dubrul, Jamar, and Crespin.[1] They covered a wide variety of activators in which qualitative observations were described, chiefly on iron, lead, chromium, nickel, manganese, uranium, neodymium, cerium, gold, copper, silver, sulfur, cadmium sulfide, and selenium. They were able to distinguish between certain glasses by their fluorescence, and they also concluded that crystallization was not necessary for fluorescence to occur.

No systematic work, however, has been done on the effect of variation of glass composition on fluorescence, and it is the purpose of this investigation to make some contribution in this field of study.

II. Experimental Arrangements

(1) Uranium in Soda-Lime-Silica Glasses and in Derived Compositions

The well-mixed batches were melted in refractory crucibles in a gas furnace at about 1350°C. under oxidizing conditions. The melting time was only long enough to complete the reaction in order to avoid as much as possible the contamination of the glass from the material of the crucible. The glass was transferred to a platinum crucible and heated in a platinum-wound furnace at 1300°C. for 24 hours in order to homogenize and fine it. It was then poured into a mold and allowed to cool on a hot brick. The glass was cut into samples, approximately 0.7 by 2.56 by 3.5 cm. in size, and heated at 400°C. for one day. Only sufficient annealing was done to give a certain degree of stability. Too much heat-treatment was avoided as some of the glasses were prone to devitrify, which might alter completely the nature of the fluorescence.

The soda-lime-silica glasses and derived compositions were prepared with potter's flint and the corresponding carbonates of the metals. Aluminum, zir-

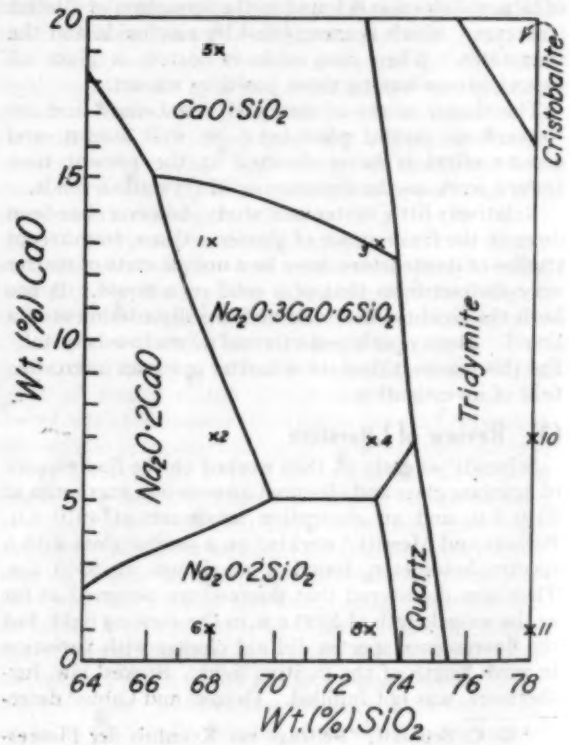


FIG. 1.—Compositions of parent soda-lime-silica glasses are denoted by crosses, superimposed on a portion of the soda-lime-silica equilibrium diagram.

[15] Alfons Schloemer, "Phosphoreszenz bei Gläsern," *Glastech. Ber.*, **11** [4] 128–29 (1933); *Ceram. Abs.*, **12** [10–11] 366 (1933).

[16] D. Dobischek, "Darstellung und Eigenschaften Lumineszenzfähiger Gläser unter Besonderer Berücksichtigung von Zinksilicat Phosphoren." Thesis, Univ. of Berlin, 1934, 39 pp.; abstracted in *Glastech. Ber.*, **13**, 370 (1935); *Ceram. Abs.*, **15** [10] 299 (1936).

[17] O. Deutschbein, "Zur Fluoreszenz Seltener Erden in Gläsern," *Z. Physik*, **102**, 772 (1936).

[18] (*a*) R. Tomaschek, "Applications of Phosphorescence Spectra to Investigation of the Structure of Solids and Solutions," *Trans. Faraday Soc.*, **35**, 148 (1939).

(*b*) R. Tomaschek and O. Deutschbein, "Über die Erschliessung der Glasstrucktur aus Fluoreszenzbeobachtungen," *Glastech. Ber.*, **16** [5] 155–63 (1938); *Ceram. Abs.*, **17** [9] 302 (1938).

[19] Hartmut Wiehr, "Über die Kristallization von Einfachen Natriumsilikat Gläser," *Sprechsaal*, **70** [12] 158–61 (1937); for abstract of series, see *Ceram. Abs.*, **16** [9] 270 (1937).

[20] W. A. Weyl, "Beitrag zur Fluoreszenz der Gläser," *Sprechsaal*, **70** [46] 578–82 (1937); *Ceram. Abs.*, **17** [10] 326 (1938).

[21] J. Rexer, "Lumineszenz von Gläsern," *Glastech. Ber.*, **16** [3] 90–91 (1938); *Ceram. Abs.*, **17** [7] 248 (1938).

conium, and titanium were introduced as oxides. Uranyl nitrate (1.86 gm., equivalent to 1% of UO_2) was added for every 100 gm. of the soda-lime-silica glass. The same amount (per 100 gm. of the equivalent soda-lime-silica glass) was added to the derived compositions, which are stated on pages 142 and 143.

The compositions of the soda-lime-silica glasses used are indicated in Fig. 1 by numbered x-marks. The base composition used for the derived compositions was point No. 2.

(2) Phosphate and Borate Glasses

The phosphate and the borate glasses were melted in refractory crucibles at about 600°C. in a gas furnace, after which they were transferred to platinum crucibles and fined at about 700°C. The glass was poured into the mold, transferred to an electric furnace at 200°C., and allowed to cool at the natural rate of this furnace.

The raw materials used for the phosphate glasses were calcium phosphate, sodium ammonium hydrogen phosphate, and ammonium hydrogen phosphate. Sodium tetraborate and boric acid were added to the borate glasses.

(3) Copper-Bearing Glasses

The batches of a series were well mixed and melted in a gas furnace with slightly reducing atmosphere. Inasmuch as the glasses were very viscous, they were heated at 1550°C. for four hours after which they were formed in the mold and allowed to cool rapidly in the air. The compositions of the potash-lime-silica glasses used as base glass for the copper are shown in Table I with their notations as 1R, 2R, etc.; 0.4% of cuprous oxide and 1.5% of stannous oxide were added as activators. Most of the raw materials used in the different glasses were of c.p. grade.

All of the glass pieces were ground to the same size, 0.6 by 2.5 by 3.2 cm. One face was polished, and the other face and the edges were ground with No. 600 Carborundum abrasive.

(4) Spectrographic Arrangement

The exciting source used was a "Contiglow" spotlight. This is essentially a mercury arc lamp provided with a reflector and a filter which eliminates the mercury lines in the visible region leaving only those in the near ultraviolet and violet. The strongest lines were 3650, 4047, and 4078 a.u., in the order of decreasing intensity.

The apparatus used for taking the spectra was a Hilger constant deviation spectrometer with photographic attachment (Fig. 2). The exciting illumination was perpendicular to the direction of the collimator tube. The sample was placed before the slit with the polished face upward toward the exciting source. The width of the specimen was crosswise with the slit of the spectrograph.

The specimen, at room-temperature determinations, was placed 2 cm. from the slit with a constant slit width of about 0.3 mm. A smaller slit width was not used because of the difficulty to get sufficient exposure, and there would be no gain in information from the resulting spectra if they consisted of wide bands. The sample was placed far enough from the slit to avoid any local irregularity on the image of the specimen that might be recorded on the spectrum. This effect was further minimized by grinding the edge facing the slit with No. 600 Carborundum abrasive. Under these conditions, the light passing through the slit was representative of the light coming from the whole specimen and not from any definite small portion.

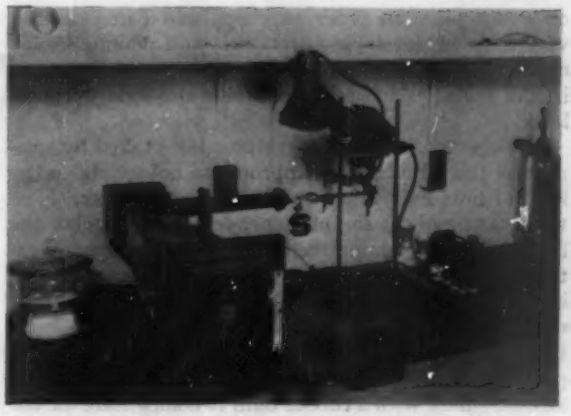


FIG. 2.—Apparatus for obtaining fluorescence spectra at room temperature; ultraviolet source, E, illuminates glass sample, S; fluorescence from S is photographed by spectrometer, P.

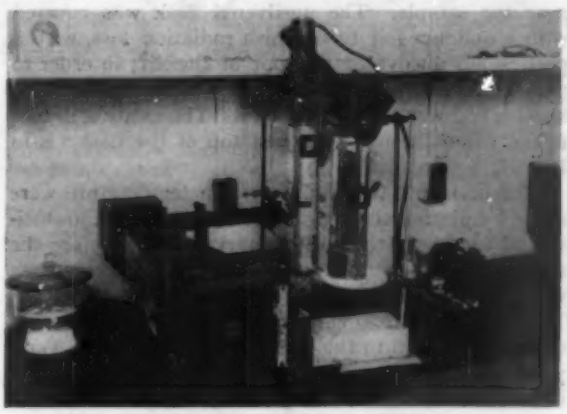


FIG. 3.—For low-temperature experiments, the apparatus shown in Fig. 2 was modified by placing the glass sample in an unsilvered Dewar flask, D, containing liquid air which was pumped over from a reservoir, D'; flask D was covered with aluminum foil except for a window, L, which permitted the fluorescent light from the sample to enter the spectrometer.

The exposures ranged from three to thirty minutes. Super Pancro Press type plates from the Eastman Kodak Company were used. The developer consisted of a DK-50 solution from the same company, and the fixer was of the formula P-5. Density determinations of the plates were made by a Leeds and Northrup microphotometer.

In a series of determinations, the exposure, developing, and fixing times were kept as nearly constant as possible in order to make quantitative comparisons. The spectrum of a standard fluorescent specimen of the same type as the samples being determined was taken

on every plate in order to check and correct slight variations in developing procedure and nonuniformity of the plates. A direct proportionality was assumed in the densities inasmuch as the variations were not large.

The spectra at low temperatures were taken by supporting the sample in an appropriate holder above the level of liquid air in an unsilvered Dewar flask. The temperature of the sample depended on the level of the liquid air which diminished continuously by evaporation. In order to keep the temperature constant during an exposure, an auxiliary Dewar flask (silvered) with liquid air was connected with the first flask by a U-bent insulated glass tube (Fig. 3). Liquid air was pumped at intervals into the original flask from the auxiliary flask with a rubber bulb to compensate for the evaporation. In this way, the liquid level was kept practically constant, and the temperature could be controlled to within 7%. The temperature was determined by a copper-constantan thermocouple placed near the sample. The unsilvered flask was covered with aluminum foil to diminish radiation loss, with a portion left uncovered in front of the slit; in order to prevent moisture from condensing on the window, a heating coil was placed around it. The exciting illumination came through the open top of the flask (*E* in Fig. 3).

Measurements taken above room temperature were made by placing the specimen inside a small Chromel-wound furnace with a fused-quartz window before the slit. A stream of air between the slit and the quartz window prevented the slit from being heated (Fig. 4). The exciting light came from the top through another quartz window into the sample in the furnace. Temperature control was maintained by a variable resistance in the circuit, and the temperature could be held constant to within 5%.

The clamps and stands holding the different accessories were furnished with table guides so that the relative positions of the specimen, spectroscope, and exciting illumination could be duplicated as closely as possible whenever it was necessary to remove any one of them.

FIG. 4.—Modification of apparatus for obtaining fluorescence spectra at elevated temperatures; electric furnace, *R*, replaces the Dewar flask, *D*, shown in Fig. 3; the glass sample is heated in the furnace and is illuminated by ultraviolet light from lamp, *E*; windows of fused-quartz glass, *Q*, are used to close openings of furnace.

The phosphorescence determinations were made by illuminating the samples first for 2 minutes with the exciting source, which was then shut off. After two minutes more, a photographic plate was placed in contact with the glowing samples for 15 seconds of exposure and at 2-minute intervals thereafter, thus giving a series of exposures as the phosphorescent light decayed. The glass specimens were placed in a box with compartments, each of which was only big enough to accommodate a sample placed sidewise with its length perpendicular. At the bottom of each compartment, strips were cut to expose the thickness of the specimens. After the specimens were excited, the box containing them was placed on top of the photographic plate, and the exposed parts of the phosphorescent glasses made the impression. The decay characteristics of all the specimens were thus taken simultaneously. After development, the blackening on the plate was measured with a microphotometer. The phosphorescence was measured after the glasses had remained in the dark for one day, inasmuch as it depended on the previous phosphorescence history of the specimen.

III. Results

(1) Soda-Lime-Silica Glasses

The variation of the fluorescence of uranium glass with composition in the soda-lime-silica field, indicated in Fig. 1, is shown in Fig. 5 (*A*), (*B*), and (*C*). These are the microphotometer tracings of the spectra of the respective glasses. Two emission bands are plainly visible. The first has its maximum at about 5300 a.u. and the second at about 5630 a.u. Schmidt[5] observed an emission maximum at 5350 a.u., and Nichols and Merritt[6] also found one maximum at 5240 a.u. These earlier investigators measured the spectra with a visual spectrophotometer, using an acetylene lamp for the comparison spectrum.

The general shape of the curves in Fig. 5 (*A*), (*B*), and (*C*) is practically the same in all of the compositions. They differ markedly, however, in intensity, which is expressed in terms of the blackening or density on the photographic plate.

The variation in intensity at the two maxima may be followed easily in Fig. 6 (*A*) to (*D*). As the lime increases, the intensity diminishes at both maxima for all silica contents used (Fig. 6 (*A*) and (*C*)). As the silica increases, the intensity of fluorescence increases at both maxima for all concentrations of lime studied.

In going from (*A*) to (*C*) on Fig. 5, it will be noticed that a third maximum begins to appear as a sharp band at 5150 a.u. as the silica content is raised; apparently, this is the weaker maximum observed by Gibbs.[8]

(*A*) *Effect of Substitutions on Fluorescence Spectra:* Figure 7 (*A*) and (*B*) represents the effect on the fluorescence spectra of uranium glass by substitutions in the soda–lime–silica system. Point 2 (Fig. 1) was taken as the base composition which corresponds to 68% of silica, 7% of lime, and 25% of soda. Equivalent amounts of lithium and potassium were substituted for

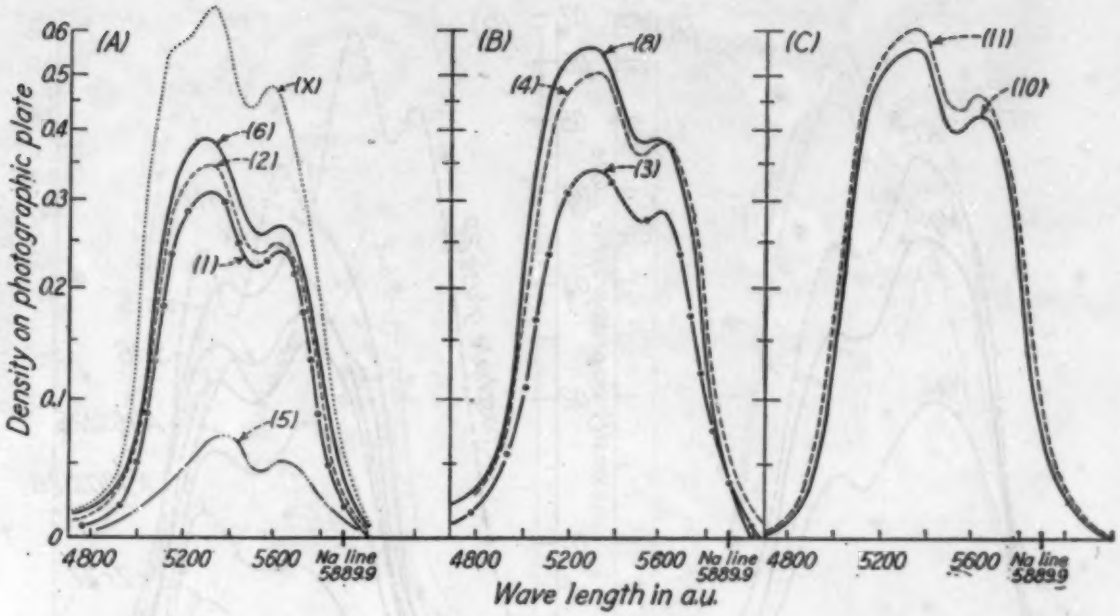


FIG. 5.—Fluorescence spectra from soda-lime-silica glasses containing 1% of UO_3; blackening of the photographic plate is a measure of the intensity of the fluorescence (ordinates); these spectra exhibit two maxima; (*A*) SiO_2, 68%; curve *X*, standard; curve 6, CaO 1%; curve 2, CaO 7%; curve 1, CaO 13%; curve 5, CaO 19%; (*B*) SiO_2, 73%; curve 8, CaO 1%; curve 4, CaO 7%; curve 3, CaO 13%; (*C*) SiO_2, 78%; curve 11, CaO 1%; curve 10, CaO 7%. Exposure time, 10 minutes in each test.

the sodium and equivalent amounts of barium, strontium, zinc, and magnesium were substituted for calcium.

The results show that the substituted glasses give similar spectra. They are unlike, however, in their intensities. In the substitution of the alkali cation, the order of decreasing intensity is potassium, sodium, and lithium. These three cations are shown to have the same order of decreasing ionic radii. The same relation is true to a certain extent in the substitution of the divalent cations. The order of decreasing fluorescence is given by zinc, magnesium, barium, strontium, and calcium. As in the alkali metals, there also seems to be a correlation between intensity of fluorescence and ionic radius. This correlation does not apply, however, all the way from zinc to calcium in the order given. The relation of ionic radius and intensity of fluorescence is clearly depicted in Fig. 8, in which the densities at the maximum, 5300 a.u., are plotted against the ionic radii. It is to be noted that zinc and magnesium belong to a different subgroup of group II from that of calcium, strontium, and barium. The relation of intensity of fluorescence and ionic radius holds within the same subgroup.

(*B*) *Effect of Substitutions for Silica:* Ten per cent of the silica content was substituted by an equivalent amount of zirconium oxide (Fig. 7 (*B*), curve 27) and the same amount by titanium oxide (curve 26); and 5 and 10% of silica were substituted by equivalent amounts of alumina (curves 25 and 26). These curves show that the fluorescence markedly decreases as silica is substituted by alumina. Substituting part of the silica by zirconia (curve 27) greatly lowers the fluorescence, and the same is true for titania substitution (curve 28).

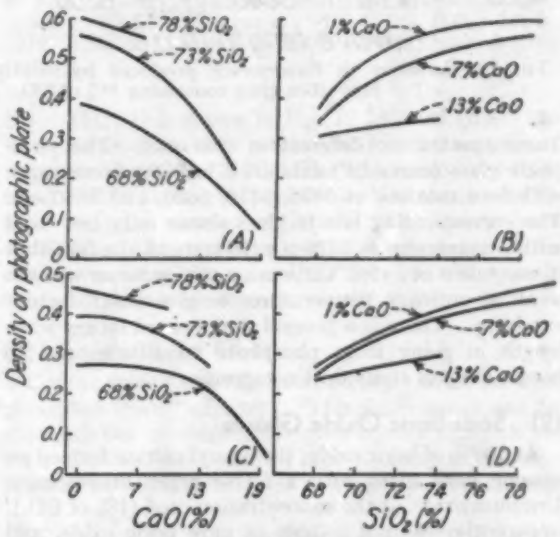


FIG. 6.—Intensity of fluorescence at two maxima shown in Fig. 5 (*A*), (*B*), and (*C*) is plotted to show its variation with composition in soda-lime-silica glasses containing 1% of UO_3; (*A*) and (*B*), variation of intensity of band at λ 5300 a.u. with composition; (*C*) and (*D*), variation of intensity of band at λ 5630 a.u. with composition.

The effect of substituting all of the silica in the glass with a composition at the same point (point 2, Fig. 1) by an equivalent amount of phosphoric pentoxide and boric oxide is shown in Fig. 9, curves 2*P* and 2*B*, respectively.

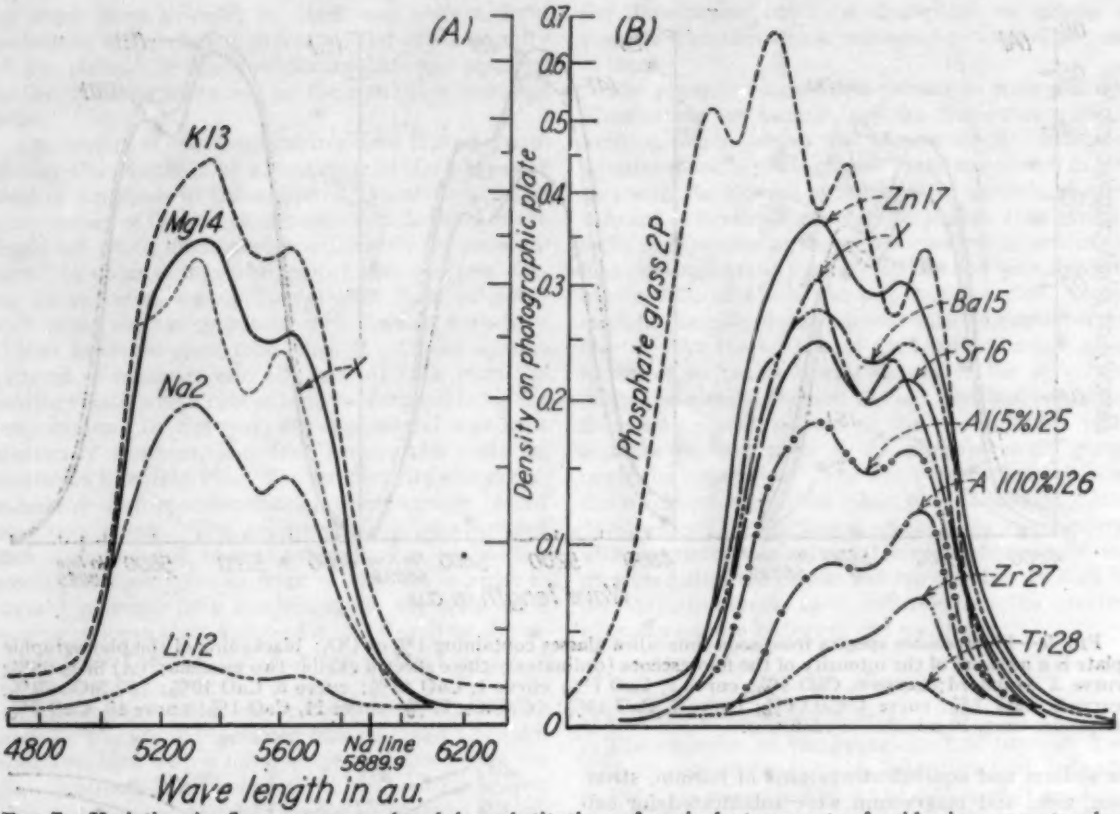


FIG. 7.—Variation in fluorescence produced by substitutions of equivalent amounts of oxides in a parent soda-lime-silica glass containing 1% of UO_2; exposure time, 5 minutes in (*A*) and (*B*).

These spectra are different in character. The phosphate glass (curve 2*P*) exhibits a brilliant fluorescence with four maxima at 5170, 5370, 5620, and 5880 a.u. The corresponding borate glass shows only one band with a maximum at 5720 a.u. in spite of the fact that it was taken at −100°C. because the emission was too weak at ordinary temperatures to give a satisfactory exposure. There is a general shift toward longer wave length in going from phosphate to silicate and to borate glass of equivalent compositions.

(2) Soda-Boric Oxide Glasses

At 100% of boric oxide, the uranyl nitrate formed an opaque dark glass with a feeble green fluorescence. Uranium oxide, at the concentration used (1% of UO_2), apparently was not soluble in pure boric oxide, and the fluorescence was too feeble to be photographed. The results in sodium borate glasses are shown in Fig. 10. At 90% of boric oxide, the glass gave a bright fluorescence with six distinct sharp bands at 4600, 4950, 5180, 5420, 5720, and 6010 a.u. As the soda was increased, the sharp bands rapidly merged into one wide diffuse band accompanied by a diminution in intensity as well as a general shift toward longer wave lengths.

(3) Soda-Borosilicate Glass

The results from the soda-borosilicate glasses are shown in Fig. 11. These spectra show the same general

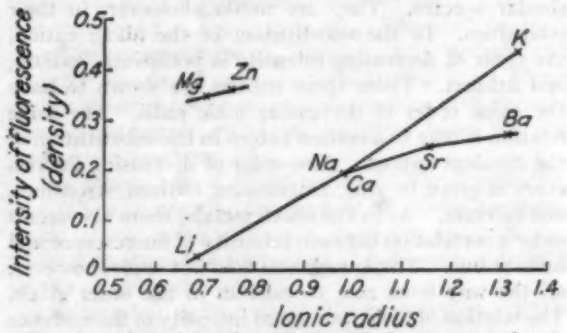


FIG. 8.—Variation of intensity of fluorescence (at λ 5300 a.u.) of glasses referred to in Fig. 7 in relation to the ionic radius of the substituting cation.

characteristic as the soda-lime-silica glasses. At 0% of B_2O_3, there is a tendency to form a third band at 5150 a.u. This band is the same one that tends to form at high silica in the soda–lime–silica system (Fig. 5 (*C*)). As the boric oxide replaces the silica, the intensity of fluorescence increases. The soda content was kept constant at 20%. The weaker maximum increases much faster than the first. The tendency to form a third band has disappeared, however, and there is a slight shift toward longer wave lengths.

(4) Effect of Temperature

The effect of temperature on the fluorescence of glass

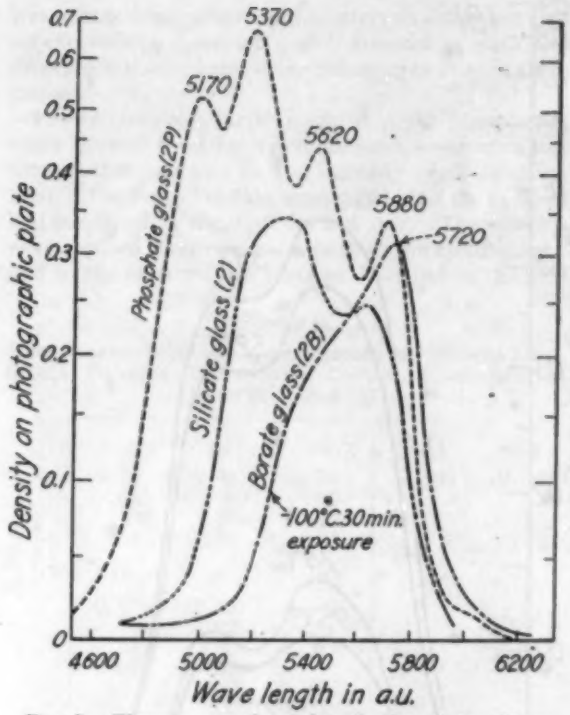


FIG. 9.—Fluorescence of uranium in phosphate, silicate, and borate glasses of equivalent compositions.

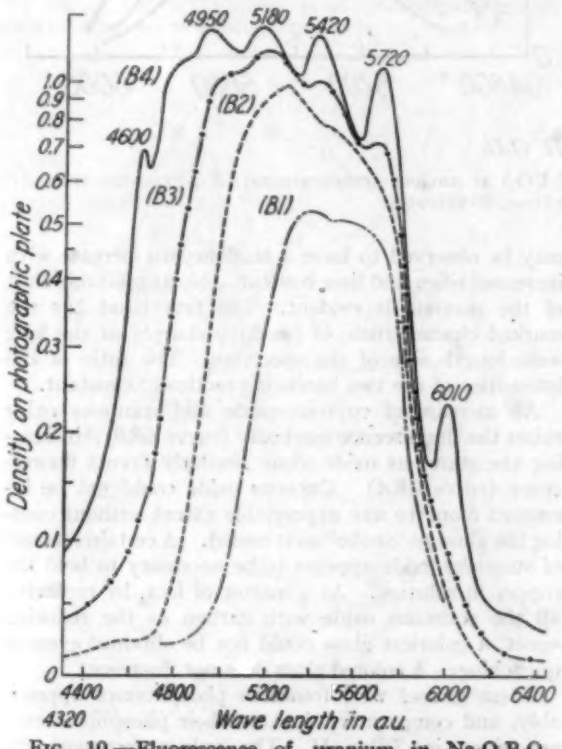


FIG. 10.—Fluorescence of uranium in Na_2O-B_2O_3 glasses; *curves:* B 1, 69.2% B_2O_3; B 2, 80% B_2O_3; B 3, 84% B_2O_3; and B 4, 90% B_2O_3; exposure time, 5 minutes.

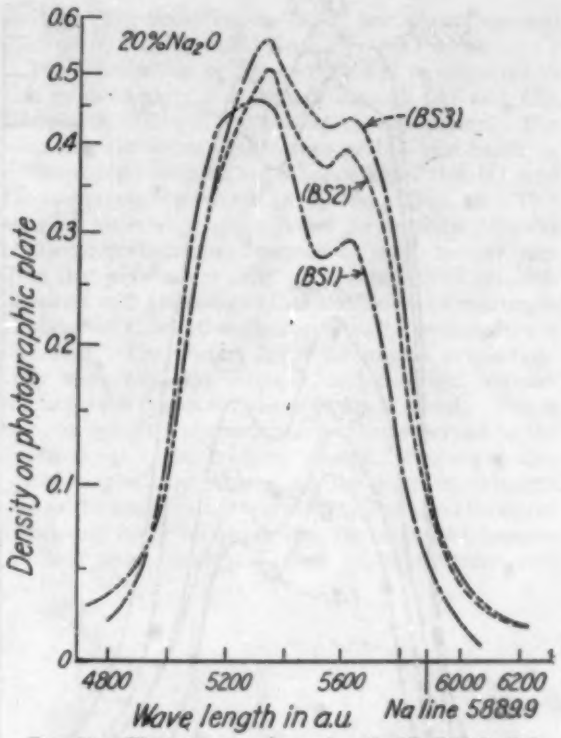


FIG. 11.—Fluorescence of uranium in Na_2O-B_2O_3-SiO_2 glasses; Na_2O, 20%; *curves:* BS 1, 0% B_2O_3; BS 2, 20% B_2O_3, and BS 3, 40% B_2O_3; exposure time, 5 minutes.

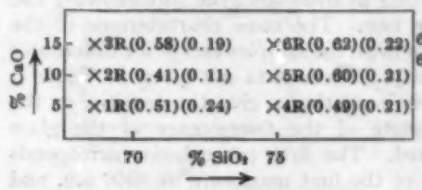
No. 1 (Fig. 1) is shown in Fig. 12 (*A*) and (*B*). The fluorescence diminishes continuously with temperature rise from −130° to 124°C. The appearance of a third band at 5220 a.u. begins to show itself at about −80°C. and is clearly seen at −130°C. The strong band at 5300 a.u. disappears proportionally faster than the weaker one at 5630 a.u., and the light emitted appears redder as the temperature is raised.

(5) Copper Ruby Glass

Copper ruby glasses fluoresce strongly when they are prevented from "striking." This fluorescence can be accomplished by cooling the glass rapidly or by choosing a glass composition with high viscosity at the temperature at which it "strikes." After several trials, this

TABLE I

COMPOSITIONS OF COPPER-BEARING GLASSES, NOS. 1R TO 6R, INCLUSIVE, MARKED BY CROSSES ON A CaO-SiO_2 GRAPH (REMAINDER, K_2O)*



* Figures in parentheses represent intensity of fluorescence at maxima of λ = 4650 a.u. and λ = 5730 a.u., respectively (see Fig. 13).

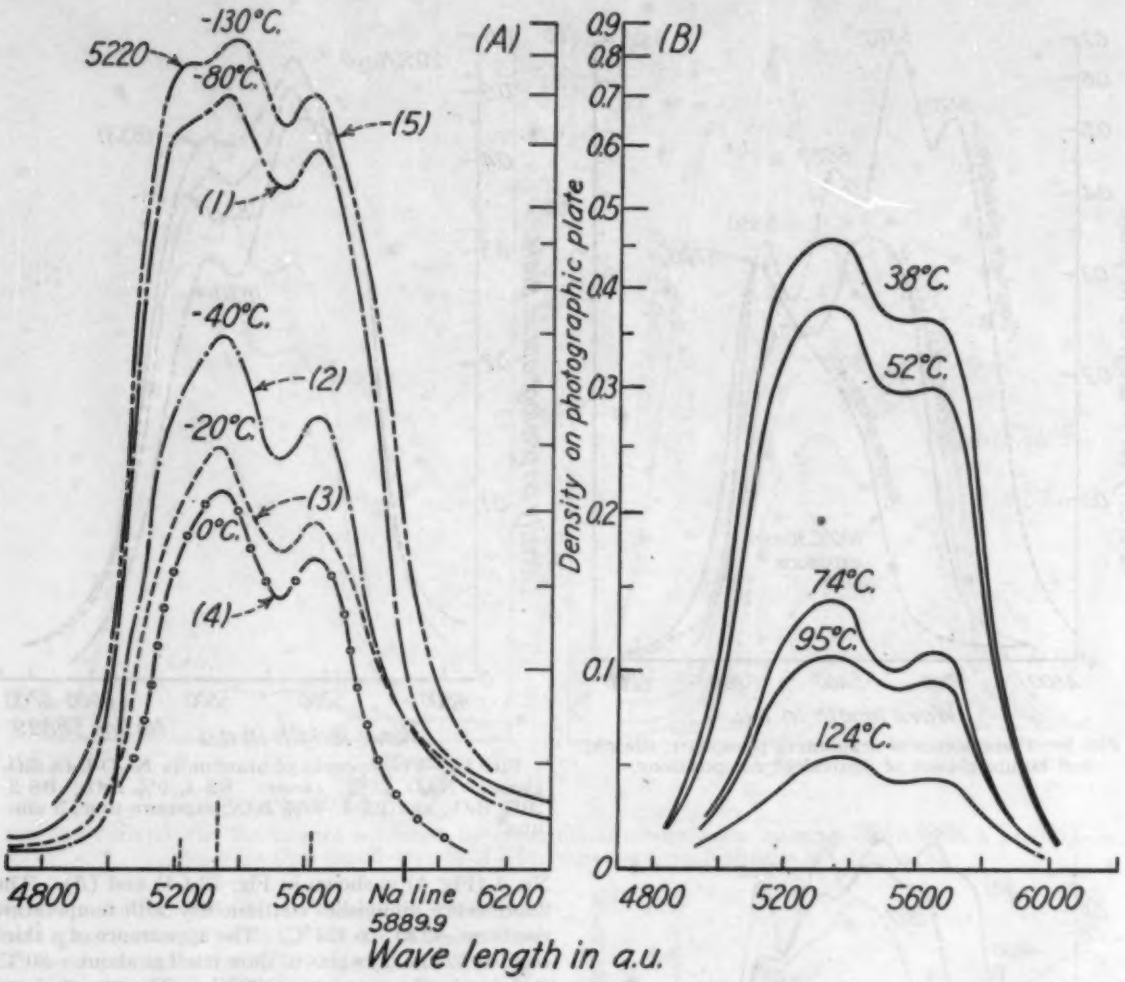


FIG. 12.—Fluorescence of uranium-bearing glasses (1% of UO_2) at various temperatures; (*A*), exposure time, 3 minutes; (*B*) exposure time, 30 minutes.

condition was obtained in potash-lime-silica glasses of the compositions shown in Table I. The points represent the composition, and their corresponding notations as 1R, 2R, 3R, etc., are shown beside them.

To each of these compositions, 0.4% of cuprous oxide and 1.5% of stannous oxide were added. Sample 6RA was similar to composition 6R, but the stannous oxide content was increased to 2.4%. Sample 6RB had the same base glass composition with 1.6% of cuprous oxide and 4.8% of stannous oxide.

The spectra of these glasses are shown in Fig. 13. Two bands are present, one showing a maximum at 4650 a.u. and the other at 5730 a.u., the former being the stronger of the two. The same characteristic of the spectra is shown in all the samples except for differences in their intensity. These data are given in Table I. The numbers in parentheses give the densities on the photographic plate of the fluorescence of the glass sample indicated. The first parenthesis corresponds to the density of the first maximum at 4650 a.u. and the second parenthesis to the density of the second maximum at 5730 a.u. As a whole, the fluorescence may be observed to have a tendency to increase with increased silica and lime content. No appreciable shift of the maxima is evident. The first band has the marked characteristic of breaking sharply at the long wave-length side of the spectrum. The ratio of the intensities of the two bands is practically constant.

An increase of cuprous oxide and stannous oxide raises the fluorescence markedly (curve 6*RB*); increasing the stannous oxide alone similarly favors fluorescence (curve 6*RA*). Cuprous oxide could not be increased alone to any appreciable extent without causing the glass to "strike" as it cooled. A certain amount of stannous oxide appears to be necessary to hold the copper in solution. As a matter of fact, by replacing all the stannous oxide with carbon as the reducing agent, a colorless glass could not be obtained even on quenching. A colored glass does not fluoresce.

These glasses were found to phosphoresce appreciably, and comparative data on their phosphorescence are given in Table II. The values represent the blackening on the photographic plate caused by the glowing samples two minutes after the exciting light

was removed and at two-minute intervals afterward with an exposure of 15 seconds each. Increase in silica and decrease in lime enhanced the phosphorescence of these glasses.

It was observed, furthermore, that the phosphorescence depended on the previous phosphorescence history of the glass and on the intensity of the exciting light. The foregoing data were taken after the samples had remained in the dark for one day. The samples were exposed simultaneously, both to the exciting light and to the photographic plate as described in the procedure. The decay curves of the best phosphorescent specimens, 4R, 5R, and 1R are given in Fig. 14.

TABLE II

PHOSPHORESCENCE AND COMPOSITIONS OF POTASH-LIME-SILICA GLASSES CONTAINING COPPER (COMPOSITIONS GIVEN IN TABLE I)*

% SiO_2	% CaO = 5	% CaO = 10	% CaO = 15
75	4R: 0.79, .245, .106, .02	5R: 0.41, .082, .028, .00	6R: 0.04, .01, .00
	6RA: 0.000	6RB: 0.000	
70	1R: 0.295, .072, .03, .005	2R: 0.19, .02, .005, .000	3R: 0.092, .01, .000

* Values represent intensity of phosphorescence at definite intervals after excitation.

The relationship of fluorescence and temperature in this type of glass is shown in Fig. 15 (*A*) and (*B*). Sample 2*R* (Table I) was used in the experiment. The intensities in terms of densities of the two bands at different temperatures are tabulated in Table III, and the corresponding curves are shown in Fig. 16. This type of fluorescent glass shows an entirely different relationship between fluorescence and temperature from that of uranium glass. The intensity of emission increases with the temperature and reaches a maximum at about 86°C. and then decreases as the temperature is increased. The weaker band diminishes proportionately more than the stronger, and the light appears whiter to the eye as the temperature is raised. This is just the opposite phenomenon to that observed in the fluorescence of the uranium glasses. The curve also becomes relatively steeper on the long wave-length side as the temperature increases. The two curves (at higher and lower temperatures) are separated because the two series were performed under different sur-

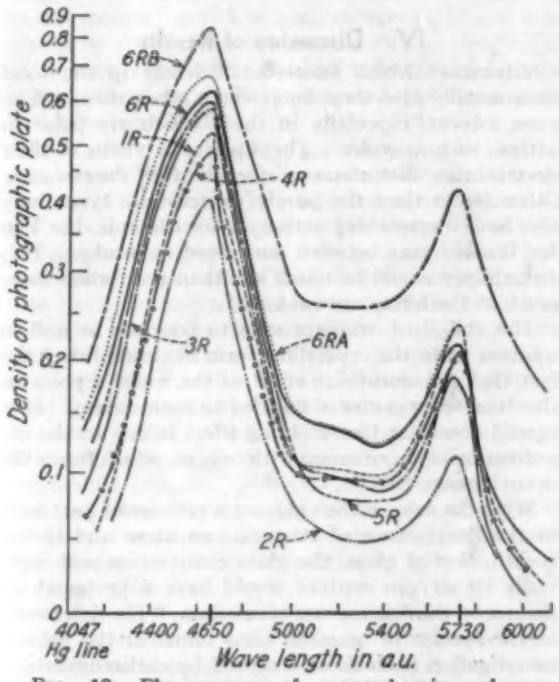


FIG. 13.—Fluorescence of copper-bearing glasses; compositions given in Table I; K_2O-CaO-SiO_2 glass containing Cu_2O and SnO as activators; exposure time, 5 minutes.

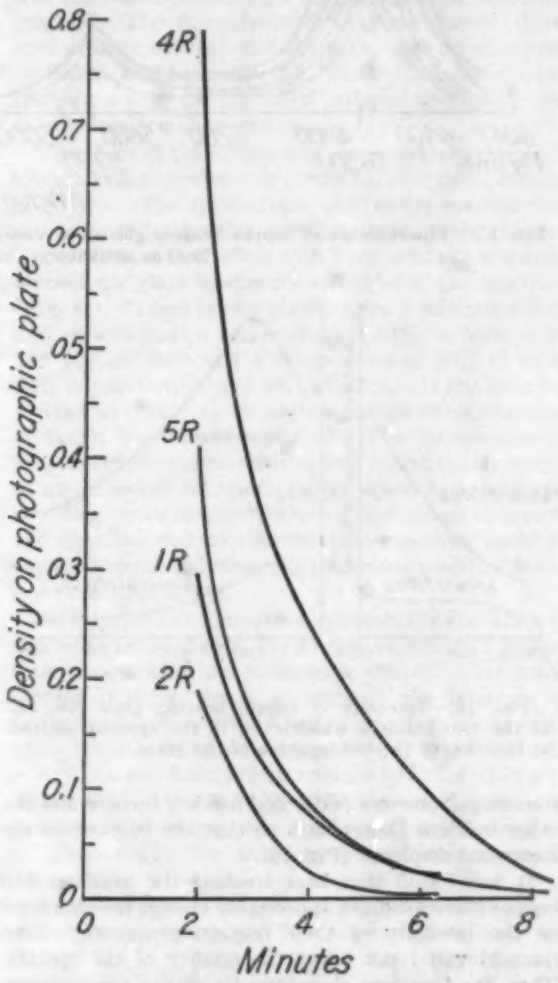


FIG. 14.—Decay of phosphorescence in copper-bearing glasses.

TABLE III

RELATION BETWEEN TEMPERATURE AND FLUORESCENCE IN COPPER-BEARING GLASS NO. 2R

Temp. (°C.)	−169	−136	−90	−68	−30	25	
Density (λ = 4650 a.u.)	0.08	0.10	0.14	0.16	0.17	0.28	
" (λ = 5730 a.u.)	0.25	0.045	0.045	0.050	0.048	0.055	
Temp. (°C.)	25	86	130	168	236	320	400
Density (λ = 4650 a.u.)	0.33	0.45	0.40	0.33	0.26	0.21	0.16
" (λ = 5730 a.u.)	0.08	0.10	0.065	0.05	0.035	0.03	0.02

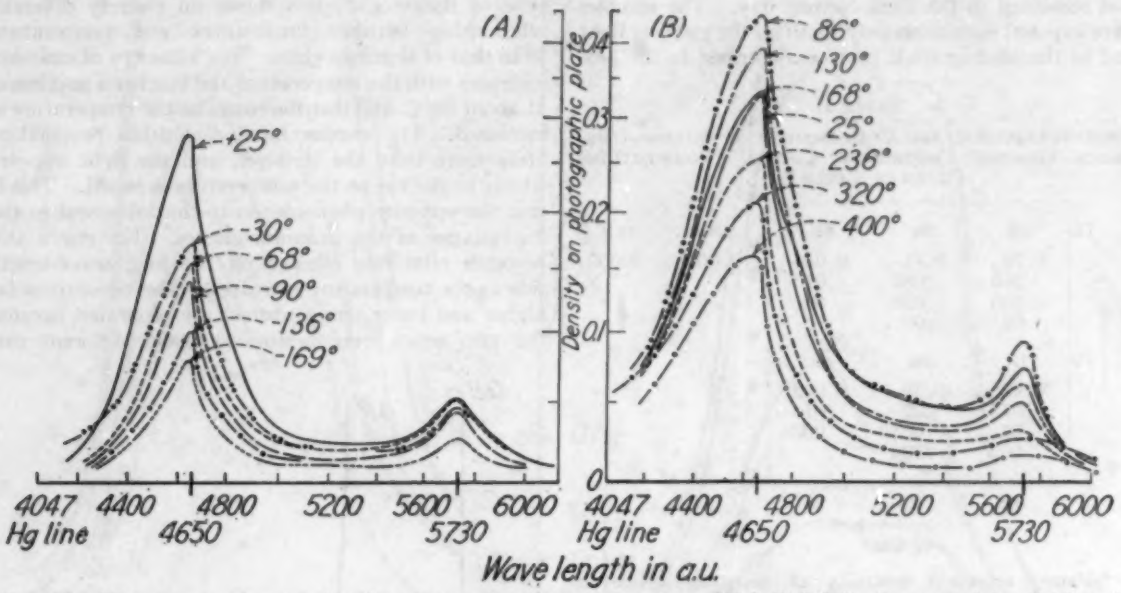


FIG. 15.—Fluorescence of copper-bearing glasses at various temperatures (K_2O-CaO-SiO_2 glass containing Cu_2O and SnO as activators); exposure time, 3 minutes.

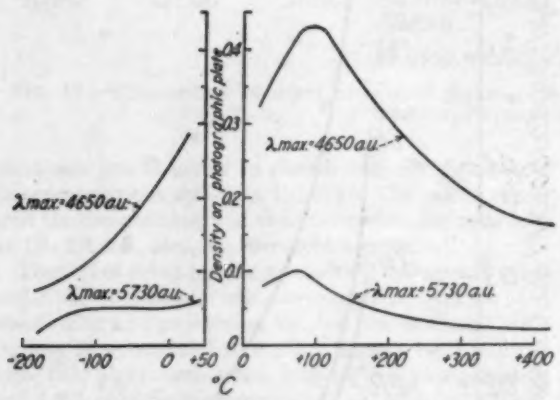


FIG. 16.—Intensity of copper-bearing glass No. 2R at the two maxima which exist in the spectra plotted as function of the temperature of the glass.

roundings; one was performed inside a furnace and the other inside a Dewar flask so that the two curves are somewhat displaced (Fig. 16).

It was found that heat treating the uranium and copper glasses did not appreciably change the character or the intensity of their respective spectra. Even quenching did not affect the quality of the spectra. They are therefore characteristic of the compositions of the glasses.

IV. Discussion of Results

Substances which fluoresce efficiently in the solid state usually lose their fluorescence when dissolved in some solvent, especially in those which are polar in nature, such as water. The dipoles, by virtue of their electrostatic disturbance, quench the fluorescence. Other forces than the purely electrostatic types may also have a quenching action as, for example, the Van der Waals forces between uncharged molecules. This disturbance would be much less than the former inasmuch as the forces are weaker.

The ability of uranium salts to fluoresce as well in solution as in the crystalline form has established the fact that the disturbing effect of the water dipoles on the fluorescing center is shielded to some extent. It is agreed now that the shielding effect is due to the coordination of the uranium with oxygen, which forms the uranyl group, UO_2^{++}.

With the oxygen thus playing a prominent part both in the fluorescence of the uranium atom and in the constitution of glass, the glass composition and especially its oxygen content would have a profound influence on the fluorescence of uranium. The differences in the spectra of uranium glass found in the present investigation from those observed by earlier investigators as presented in the results no doubt occur from the differences in the glass composition to which the earlier investigators seem not to have given much attention.

The recent concept of glass is a skeleton of oxygen atoms linked together by such primary cations as silicon, boron, or phosphorus which, with the oxygens, form groups of tetrahedrons or triangles and together form a random network. In the holes of the network are located the so-called secondary cations such as calcium, sodium, potassium, etc.

On the basis of such a concept, the variation of fluorescence with composition may be explained. The electrostatic field in the glass structure increases with the addition of secondary cations, which are ionic in nature in the glass. This increase is shown by the fact that they are easily electrolyzed. Their electrical fields, unlike the primary cation, are consequently undirected and spread in all directions. Increase of the secondary cation will therefore increase the electrical disturbance on the fluorescing uranyl group or, perhaps, on a group with more oxygen content. This would be manifest as a change in intensity (usually a decrease), a shift, and a widening of the fluorescence bands. The results of the present experiments agree with this view. The emission increases as the alkali content is lowered. A third band, furthermore, begins to appear at 5150 a.u. as the silica content is increased, which is an indication of more structure and therefore of less disturbance from its surroundings. This increased structure occurs because the disturbing secondary ions are diminished.

Along the alkali line at constant silica content, the replacement of sodium oxide by calcium oxide causes a marked diminution in the intensity of emission and a tendency for the maxima to shift toward longer wave length. This may be due to the fact that the monovalent sodium ion with an ionic radius of 0.98 a.u. is replaced by the divalent calcium ion with an ionic radius of the same value. The disturbing electrical field in the lattice, therefore, is increased, and the fluorescence would be less efficient.

That the change in electrostatic conditions within the network affects the fluorescence is clearly shown in the case of the substitution of potassium and lithium for the soda in a soda-lime glass. The ionic radii of these metals vary a great deal. Potassium has an ionic radius of 1.33 a.u., sodium has 0.98 a.u., and lithium has 0.68 a.u. The electrostatic field around the lithium ion therefore is strongest because of its small ionic radius. This property of lithium is familiar in aqueous solutions where the lithium ion is known to be heavily hydrated. That there is some correlation between ionic radii of the secondary cations and fluorescence is shown in Fig. 8. There is, however, a discrepancy in the behavior of magnesium and zinc, which do not form a continuous series with the other ions of the same valence type as do calcium, strontium, and barium. Magnesium and zinc, however, belong to a different subgroup from calcium, strontium, and barium in the Periodic Table.

The substitution of the silica by alumina, zirconia, and titania causes a marked diminution in the fluorescence of the glass. The substituting cation probably acts more in the nature of a secondary cation than as a network former. The fluorescence in this case again diminishes with decrease in ionic radius or increase in the electrical field around the ion of the valence type. Zirconium has an ionic radius of 0.79 a.u., whereas titanium has 0.62 a.u., and the intensity of emission is greater when zirconium is used than with titanium.

Because uranium has a strong coordinating tendency for oxygen, an increase in the oxygen content of the glass without increasing the interfering secondary cation might bring about a thicker protecting oxygen sheath. This means that the greater the amount of oxygen furnished by the primary cation the less would be the hindrance on the fluorescing center and the richer would be the structure of its spectrum. This is actually the case when a change is made from a silicate to a phosphate glass of the same secondary cation content (Fig. 9). The reverse effect would occur in a change from a silicate to a borate glass. Every boron atom furnishes on the average only 3/2 oxygen, every silicon 2, and every phosphorus 5/2 oxygen atom. The fluorescence of the borate glass is actually the weakest of the three (Fig. 9) and the poorest in structure. Its spectrum was taken at a low temperature inasmuch as the emission was too feeble at ordinary temperatures to be photographed. The fluorescence of uranium glasses, therefore, is more efficient the larger the amount of oxygen furnished by the primary cation because the oxygen content would be increased without increasing the interfering secondary cations.

The effect of the influence of the secondary cations in silicate glasses is also true in the borate glasses studied (Fig. 10). The fluorescence diminishes markedly in intensity and structure with increasing soda content. The replacement of silica with boric oxide in a sodium borosilicate glass lessens the structure of the spectrum (Fig. 11). These borate glasses show a minimum thermal expansion at a composition of 84% of boric oxide and 16% of soda and a composition of 20% of soda, 22% of boric oxide, and 58% of silica. It has been explained as occurring through a change in coordination of boron from three to four.[22] The fluorescence of uranium in glass apparently cannot detect these changes of coordination, inasmuch as the spectra of the corresponding series of glasses show a continuous change in one direction and no characteristic spectrum could be attached to the influence of a particular coordination in the glass structure.

An increase in temperature increases the amplitude of the vibrations between the atoms, resulting in greater interference with the fluorescing center. This interference is shown by a lowering in the intensity of fluorescence and also by a loss in structure of the spectrum (this is indicated in Fig. 12 (*A*) and (*B*)). At −80°C., a new band begins to show at about 5150 a.u., and at 124°C., the two distinct bands seen at room temperature begin to merge. The fluorescence of this type of glass diminishes continuously with increase in temperature.

A type of glass with peculiar properties of its own is the copper ruby glass. The colored glass does not

[22] J. Biscoe and B. E. Warren, "X-Ray Diffraction Study of Soda Boric Oxide Glass," *Jour. Amer. Ceram. Soc.*, **21** [8] 287–93 (1938); see p. 291.

fluoresce, but if the color or the development of the colloidal particles is prevented by cooling the glass rapidly, a luminescent glass results. The same effect may be obtained by less drastic cooling of a base glass of high viscosity.

In his work on silver glass, Weyl[20] developed fluorescence in a quenched silver glass by reduction with hydrogen, and he concluded that the fluorescing center is the silver atom. The same effect was obtained by reduction of other silver preparations. Because silver and copper ruby glasses are of the same nature, the fluorescing centers in copper ruby glasses are probably the copper atoms or at least a very small group of copper atoms.

The shape of the strong band at 4650 a.u. (Fig. 13) shows that the energy band of the excited state is much wider than that of the ground state. This would be true if the fact is considered that the electrons are detached from the excited atom and wander in the glass lattice. A detached electron would be capable of assuming a wider range of continuous energy than a bound electron. A drop from this wide energy band to a narrower one below will result in the sudden drop of the band toward longer wave lengths. The phosphorescence of the glass also lends support to this view. The free electrons will encounter obstacles in going back to the original ground state which would show as an afterglow. The glasses which have a good phosphorescence have a low fluorescence (Table I). This is mainly the result of a difference in the rapidity in which the electrons drop to the ground state. Electrons which are trapped in a metastable state cannot go to the ground state easily, and this will be shown as phosphorescence.

A peculiar property of this type of luminescent glass is the temperature relationship, which shows a maximum at about 86°C. (Fig. 16). It is reasonable to expect that not only individual copper atoms are present but also small groups of copper atoms which act as fluorescing centers. This condition would still leave the glass colorless. Because not enough atoms are grouped to form a crystal unit, they will probably be held by weak forces. Raising the temperature would expand the glass structure, thus allowing greater freedom of the fluorescing centers and therefore less disturbance from its surroundings, a condition favorable for emission. Further increase in temperature would bring into prominence the thermal vibrations of the surrounding medium, in this way creating a condition unfavorable for fluorescence. Under these conditions, a maximum would be exhibited as the temperature is raised.

Furthermore, as the temperature is raised, the longer wave lengths disappear proportionately faster than the shorter. At 400°C., the weaker band at 5730 a.u. has almost disappeared. This shift toward shorter wave length with rise in temperature is not common. A fluorescence spectrum usually shifts toward longer wave lengths such as occur in the uranium glasses. This phenomenon may indicate that as the temperature rises the groups dissociate into individual atoms which are capable of emitting in the shorter wave lengths.

It is also to be noted that, as the temperature is raised, the curve becomes relatively steeper at the long wave-length side (Fig. 16), which means that the energy band of the excited state becomes relatively wider compared to that of the lower state. The existence of the copper in the atomic form makes it probable that its excited state gives off free electrons. It would be interesting to measure the photoconductivity of this type of glass.

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An old problem

RELATION OF HYDROGEN TO ADHERENCE OF SHEET-STEEL ENAMELS*

By W. A. Deringer

Abstract

The principal theories of adherence are reviewed, and a new theory involving hydrogen gas is discussed. A review of the literature and experimental data show that hydrogen is a factor in the adherence of sheet-steel enamels and that adherence, reboiling, and fish scaling are closely related.

I. Introduction

Numerous articles recorded in ceramic literature discuss investigations of enamel adherence to sheet iron and are proof that this phenomenon is perplexing. Enamelers have known for many years that cobalt oxide, nickel oxide, or both were necessary ingredients of sheet-iron, ground-coat enamels. They learned this by experience without finding any satisfactory reason for its being so. This phenomenon was investigated from time to time, and although the literature is replete with theories concerning the adherence of sheet-iron, ground-coat enamels, the proofs are inadequate and contradictory. The four principal theories advanced by past investigators have been summarized by Kautz[1] as follows:

(1) The gripping theory maintains that enamel glass is held to the metal by inclosing the projections and filling the depressions occurring on the metal surface.

(2) The electrolytic theory is based on the supposition that iron, being higher in the electrochemical series of the elements, will displace or plate out cobalt and nickel in solution in the ground-coat enamels. These plates of cobalt and nickel adhere to the iron; the enamel glass is mechanically bonded to the metal plates by gripping and by dendrites.

(3) The dendritic theory contends that tiny, toothlike crystals of alpha iron, or ferrite, are crystallized from the solution of iron oxide in the glass and become attached to the iron base, thus literally "spiking" the glass to the base in numerous places.

(4) The oxide-layer theory maintains that the glass is held to the iron by an intervening layer of iron oxide.

Howe[2] more recently proposed a different theory. He says, "... the adherence of a sheet-iron ground coat to enameling iron is due to an oxidation of the iron with subsequent solution in the enamel to form what might be termed a solution or chemical union bond." Since the last published articles on enamel adherence, Zapffe and his associates[3] have shown the important role that hydrogen has played in many enamel defects.

It is the purpose of the author to show the relation of hydrogen to the adherence of sheet-iron ground coats in view of these recently published articles which describe the behavior of hydrogen in iron.

II. Hydrogen Theory of Adherence

In a search for a better explanation of the adherence phenomenon, the author was attracted by the anomalous phenomenon of the adherence of porcelain enamel to copper. As far as is known, there is no complicated explanation for the adherence of enamel to copper; it simply adheres to the copper base metal by a gripping action without the complicated chemical or physicochemical reactions which have been considered essential to bond enamel to sheet iron. Yet the surface of copper is prepared for enameling in the same manner that iron is prepared, and the same compositions may be used for enameling both copper and iron. It would seem, then, that there need be no complicated explanation for the adherence of enamel to iron.

The fact that cobalt oxide must be present in sheet-iron, ground-coat enamels indicates that there is a difference between the bonding of enamel to iron and to copper. Past reasoning has followed along the general lines that there must be some bonding medium to hold the glass to the iron. According to Kautz,[1] this bonding medium is ferrous oxide; King[4(d)] and his associates state that the bonding medium includes dendrites of alpha iron; and Staley[5] says that enamel is bonded to the base metal by a thin layer of metallic cobalt or nickel.

The present author has proposed a theory in which porcelain enamel has inherent adherence for iron just as it has for copper, whether or not cobalt oxide is present in the glass, and the difference between adherence to copper and iron is caused by some property associated with iron that is not associated with copper.

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* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943 (Enamel Division). Received December 26, 1942.

Submitted in partial fulfillment of the requirements for the degree of Master of Science (Metallurgical Engineering), University of Wisconsin, Madison, Wis., 1943.

[1] Karl Kautz, "Further Data on Enamel Adherence," *Jour. Amer. Ceram. Soc.*, 19 [4] 93–108 (1936).

[2] E. E. Howe, "Observations on Adherence Phenomena of Sheet-Iron Ground Coats," *Better Enameling*, 9 [9] 13–19 (1938); *Ceram. Abs.*, 19 [8] 183 (1940).

[3] (*a*) C. A. Zapffe and C. E. Sims, "Relation of Defects in Enamel Coatings to Hydrogen in Steel," *Jour. Amer. Ceram. Soc.*, 23 [7] 187–219 (1940).

(*b*) C. A. Zapffe and J. L. Yarne, "Relation of Surface Oxidation to Certain Defects in Enamel Coatings on Steel, III," *ibid.*, 25 [April 1, No. 7] 191–94 (1942).

[4] (*a*) G. H. Spencer-Strong and R. M. King, "Mechanics of Enamel Adherence: V, Study of Enamel-Metal Contact Zones by Chemical Methods," *Jour. Amer. Ceram. Soc.*, 15 [9] 480–83 (1932).

(*b*) Karl Schwartzwalder and R. M. King, "Mechanics of Enamel Adherence: VI, Petrographic, Metallographic, and X-Ray Study of Enamel-Metal Contact Zones," *ibid* pp. 483–86 (1932).

(*c*) G. H. Spencer-Strong, J. O. Lord, and R. M. King, "Mechanics of Enamel Adherence: VII, Further Studies of Enamel-Metal Contact Zones by Microscopic and Metallographic Methods," *ibid.*, pp. 486–90 (1932).

(*d*) R. M. King, "Mechanics of Enamel Adherence: X, 'Iron Oxide Layer' in Sheet-Steel Ground Coats," *ibid.*, 17 [7] 215–19 (1934).

[5] H. F. Staley, "Electrolytic Reactions in Vitreous Enamels and Relation to Adherence of Enamels to Steel," *ibid.*, 17 [6] 163–67 (1934).

This difference in the behavior of copper and iron is thought to be caused by hydrogen gas in the iron. The peculiar behavior of hydrogen in steel is described in detail in many published articles by Zapffe[6] and his associates, and it is known that the hydrogen–copper system does not exhibit such properties. Figure 1 shows that copper does not have the tremendous increase in hydrogen solubility with increasing temperature which is characteristic of iron. The most outstanding difference in the behavior of hydrogen to iron and copper is the diffusion rate of atomic hydrogen through these metals. Although nascent hydrogen readily passes through iron even at room temperature, copper is impermeable to this gas.[7]

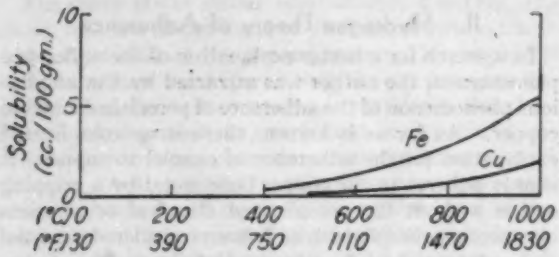

FIG. 1.—Hydrogen solubilities (after Smithells[7]).

Hydrogen evolved during the firing of enamel on sheet iron acts as a barrier between the base metal and the enamel; it is an intermediate layer which blankets the metal surface in such manner as to prevent the glass from wetting the metal and adhering to it. The presence of the iron oxide layer at the interface indicates that the hydrogen has been removed by oxidation to water which dissolves in the glass layer.[8] An absence of the oxide layer at the interface is characteristic of poor adherence and indicates a reducing condition (hydrogen) at the interfacial surface. An excess of iron oxide at the junction of the base metal and enamel also indicates poor adherence because of the mechanical weakness of iron oxide as a bonding medium. The proper amount, neither too much nor too little, of iron oxide is thus necessary to develop adherence. One of the functions of the cobalt oxide in the glass is to act as an oxygen carrier[9] in maintaining the delicate balance required to give the amount of iron oxide at the interface necessary to oxidize the hydrogen.

III. Literature Review

In reviewing the literature on the adherence of sheet-iron enamels, it is concluded that there must be some relationship between adherence and the phenomenon of reboiling. Zapffe and Sims[3(a)] give a detailed and comprehensive explanation of the reboiling phenomenon. Their theory, based on hydrogen gas evolution as a cause of reboiling, explains practically all of the many unusual factual data enumerated by Lord.[9] This is something none of the other investigators have been able to do. Because of this theory, it is interesting to review some of the previously published articles on reboiling.

Lord[9] associated the adherence oxides of cobalt and nickel with reboiling; "reboiling takes place only on cobalt (and possibly nickel) ground coats and only on sheet steel." He thus intimated that the gas which causes reboiling depends on the adherence oxides for its presence. He also states that possibly the explanations of adherence and reboiling will be found to be the same.

The presence of cobalt oxide in the frit could scarcelp account for the reboil bubbles. It seems reasonable, therefore, that the gas is present even when the adherence oxides are absent, but instead of revealing itself as reboil bubbles, the gas may be present in some other form or in some other place. The writer contends that these statements by Lord strengthen the argument that both adherence and reboiling phenomena are controlled by the presence or absence of hydrogen gas in the iron base metal.

Howe and Fellows[10] also found that reboiling was closely related to adherence and that any metallic oxide which increased the adherence also increased the reboiling tendency.

Geisinger and Berlinghof[11] called attention to the fact that hydrogen and water vapor produce bubbly enamels with poor bond. These authors contend that the main feature desirable for good adherence is a rough metal surface, that bonding is chiefly a mechanical phenomenon, and that enamel composition and atmosphere are only of secondary importance.

It is interesting to note that both hydrogen and water vapor produce poor bond. The water vapor at enameling temperatures decomposes to give atomic hydrogen, and regardless of whether the hydrogen is present in the furnace as such or is present as a result of the decomposition of water vapor, the result is the same, namely, bubbly enamel and poor adherence.

Kautz[12] concluded that the iron oxide film, which forms between the enamel layer and the iron base definitely affects the adherence of the enamel. He realized the importance of having an oxidizing condition at the interface by stating, "A well-balanced ground coat should have the proper amounts of adherence-promoting oxides incorporated in it so that a fairly heavy iron oxide film is maintained between the enamel and iron during firing."

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[6] C. A. Zapffe and C. E. Sims, "Hydrogen Embrittlement, Internal Stress, and Defects in Steel," *Trans. Amer. Inst. Mining Met. Engrs., Iron Steel Div.*, **145**, 225–61 (1941); discussion, pp. 261–71; *Metals Tech.*, **8** [August], 37 pp., 1941; *Tech. Pub.*, No. 1037. See also footnote 3.

[7] C. J. Smithells, Gases and Metals, pp. 125 and 159. John Wiley & Sons, Inc., New York, 1937. 218 pp.

[8] A. E. Badger, "Seeds in Soda-Lime Glass," *Ceram. Ind.*, **27** [1] 17–21 (1936); *Ceram. Abs.*, **16** [9] 272 (1937).

[9] J. O. Lord, "Summary of Observations and Facts Concerning Phenomenon of Reboiling," *Jour. Amer. Ceram. Soc.*, **16** [9] 442–51 (1933).

[10] E. E. Howe and R. L. Fellows, "Effect of Manganese, Nickel, and Cobalt on Adherence and Reboiling Properties of Ground-Coat Enamel," *ibid.*, **20** [10] 319–24 (1937).

[11] E. E. Geisinger and K. Berlinghof, "Effect of Furnace Gases on Glass Enamels," *ibid.*, **13** [2] 126–42 (1930).

[12] Karl Kautz, "Observations on Function of Adherence-Promoting Oxides in Ground-Coat Enamels," *ibid.*, **22** [8] 250–55 (1939).

Kautz[13] also found that gases evolved from commercial sheet iron when heated are of such reducing nature and quantity as to cause red cuprous oxide, metallic copper, or both to form from glasses containing cupric oxide. He stated, furthermore, that gases evolved from commercial sheet iron when heated are of such quantity and reducing nature as to cause metallic iron (and probably metallic nickel) to be reduced from thick layers of commercial ground-coat enamels fired on iron.

These observations fit in nicely with the observation that lack of adherence of enamel to iron is accompanied by a shiny metal surface, that is, a reducing condition at the interface, which could reasonably be caused by the evolved reducing gases mentioned by Kautz.

In experimenting with enameling of various metals, Kautz[1] found that enamel would adhere satisfactorily to copper, silver, gold, and platinum and to 18–8 stainless steel but not to 15% chromium stainless steel. On all of the precious metals and on copper, the adherence of the enamel was good whether or not the metal was preoxidized, whereas chromium, nickel, ferro-chrome, iron, and the 18–8 stainless steel showed improved adherence if the pieces were preoxidized before firing.

Kautz thoroughly justified his theory that an iron oxide layer was necessary for enamel adherence, but he attributed the adherence directly to the oxide layer rather than to the fact that an oxide layer signified the absence of a reducing condition at the interface.

In describing one of their experiments, Zapffe and Sims[3(a)] told about effusing hydrogen which caused enamel to explode away from the metal base. They also stated, ". . . the evolution of hydrogen was so severe during firing that no oxidation and no bonding occurred." The authors were associating poor adherence with the presence of hydrogen and the lack of an oxide layer.

In another article,[3(b)] Zapffe and Yarne show that it is possible to secure a good adhering coating of enamel without the use of cobalt oxide if a tightly adhering oxide is first secured on the base metal. The authors list the following advantages of preoxidation:

> Such preoxidation serves most of the purposes of a ground coat. There should be some additional advantages for the following reasons: (1) Good adherence, which is largely a function of an interfacial layer, may be developed as well (or better) when the oxide is preformed under controlled conditions as when it is developed during enamel firing by miscellaneous reactions of the iron with moisture in the enamel coating and with gases in the atmosphere. (2) The variable and often important quantity of inherent hydrogen in enameling stock, which is present in the steel when it is received from the mill, would be uniformly decreased, perhaps in critical amounts, by the oxidation treatment when it is conducted in a suitable moisture- and hydrogen-free atmosphere. The chance factor of hydrogen-caused defects appearing anomalously in different lots of steel would thereby be reduced. (3) The hydrogen pick-up during enameling would be largely eliminated because no pickling, neutralizing, rinsing, or nickel dipping would be required; nor would there be reboiling, fish scaling, and such defects as are often caused by hydrogen absorption during the firing of the first coat.

These authors stress the importance of an oxide layer at the interface as the prime factor in producing good adherence, whereas the writer contends that the absence of a reducing condition (hydrogen) at the interface is the reason that the enamel adheres to the preoxidized base metal.

IV. Experimental Studies

In order to gather evidence in connection with this theory, a number of experiments were carried out.

(1) Presence of Gas at Interface

Two strips of copper, 1 in. by 6 in. by 18 gauge, and two similar strips of enameling iron were sandblasted and enameled according to the procedure shown in Table I.

TABLE I

Specimen	Base metal	Enamel
A	Iron	X
B	"	Y
C	Copper	X
D	"	Y

Composition Y was an ordinary commercial ground-coat enamel, and composition X was the same enamel except that it contained no cobalt oxide, nickel oxide, or manganese dioxide. These pieces were fired in air for four minutes at 1600°F. On cooling, the enamel on specimen A separated from the base metal giving a splotched appearance, the splotches being areas where the enamel was completely separated from the base metal (Fig. 2). None of the other specimens showed this condition. Microscopic examination revealed that gas bubbles rose from the punctures if these splotches were pricked by a sharp point while the specimen was immersed in water. No formation of these bubbles occurred when the enamel surface was punctured in the area between the splotches, which indicated that the splotches were actual separations between the enamel and the base metal, that is, separations with considerable gas pressure.

The four strips were then bent into U shapes and were immersed in a beaker of water. Specimen A showed a

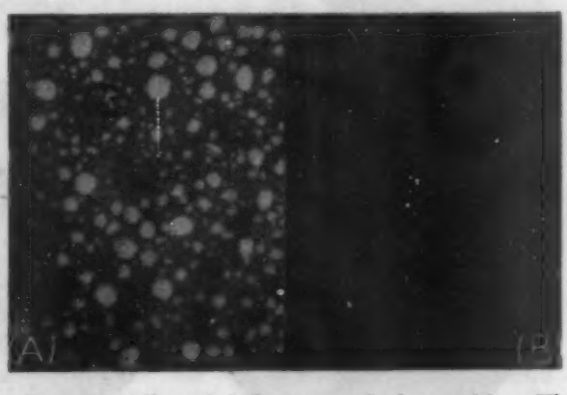

FIG. 2.—(*A*), cobalt-free enamel (composition X) showing splotches, an indication of poor adherence; (*B*) commercial ground-coat enamel (composition Y), showing absence of splotches.

[13] Karl Kautz, "Random Experiments on Enamel Adherence," *Jour. Amer. Ceram. Soc.*, 21 [9] 303–307 (1938).

considerable evolution of gas from the areas where the glass cracked from the piece. On the compression side, the glass broke off violently in flakes which were projected from the base metal with considerable force. As each flake separated from the piece, a train of tiny bubbles rose to the surface from the point of separation. On the tension side, the cracks in the glass were marked by rows of tiny gas bubbles superimposed on the cracks. Specimen B showed a slight gas evolution, whereas specimens C and D gave off no gas whatsoever.

An examination of the base metal of each specimen at the fracture showed that the shiny base metal was exposed on specimen A but that some form of coating was present on the metal surface of each of the other pieces. In the case of the two copper pieces, the substance at the interface appeared to be red copper oxide, whereas the substance in specimen B was dark gray to black in color and appeared to be ferrous oxide. When the porcelain enamel adhered to the iron, as on specimen B, an oxide film was present at the interface. In the case of the poorly adhering coating of enamel on iron, no such oxide layer occurred, and the base metal was shiny where the glass had been broken away. A mildly oxidizing (FeO) condition evidently was present at the interface of specimen B and a reducing condition at the interface of specimen A. Hydrogen gas ranks high as a reducing agent, and it is an ever-present constituent in steel[3(e)] and in the chemically combined water of the clay used in suspending porcelain enamel.[14] It is natural to conclude, therefore, that the initial oxide layer produced in the early stages of firing on specimen A was reduced back to elemental iron during a later stage of the firing operation. The cobalt oxide present in the enamel, however, acted as an oxygen-carrier[12] on specimen B and continued to supply sufficient oxygen through the molten glass layer to prevent the reduction of ferrous oxide.

It was considered advisable to refine the procedure for evaluating the gas evolution from fractured enamel coatings so that determinations could be made, at least roughly, on the relative quantities of gas evolved from plates enameled similarly to specimens A, B, C, and D. After preliminary trials, 18-gauge specimens, $1/2$ by $4\,1/2$ in. in size, were sheared from enameling iron and from a rolled copper sheet. They were then bent into the form shown at the top of Fig. 3 and were sprayed, dried, and fired in the usual manner. Three specimens were used; specimen A consisted of enameling iron coated with cobalt-free, ground-coat enamel; specimen B was enameling iron coated with a cobalt ground-coat enamel; and specimen C consisted of copper coated with cobalt-free, ground-coat enamel. Each enameled piece was immersed in a large pan of distilled water. A thoroughly cleaned four-inch watch glass was inverted in the pan of water and held in position underneath the surface of the water. Care was taken to prevent entrapment of air bubbles under the watch glass. With a pair of pliers in each hand, the specimen was gripped at each end and was carefully bent and distorted under the watch glass until the specimen appeared as shown in the middle of Fig. 3. The gas, released when the enamel was ruptured, rose and collected on the under side of the watch glass. The watch glass, with

[14] H. Hoff and J. Klärding, "Correlation Between Gas and Fish-Scale Formations in Enameling," *Stahl & Eisen*, 58, 914–16 (1938); *Ceram. Abs.*, 18 [5] 121–22 (1939).

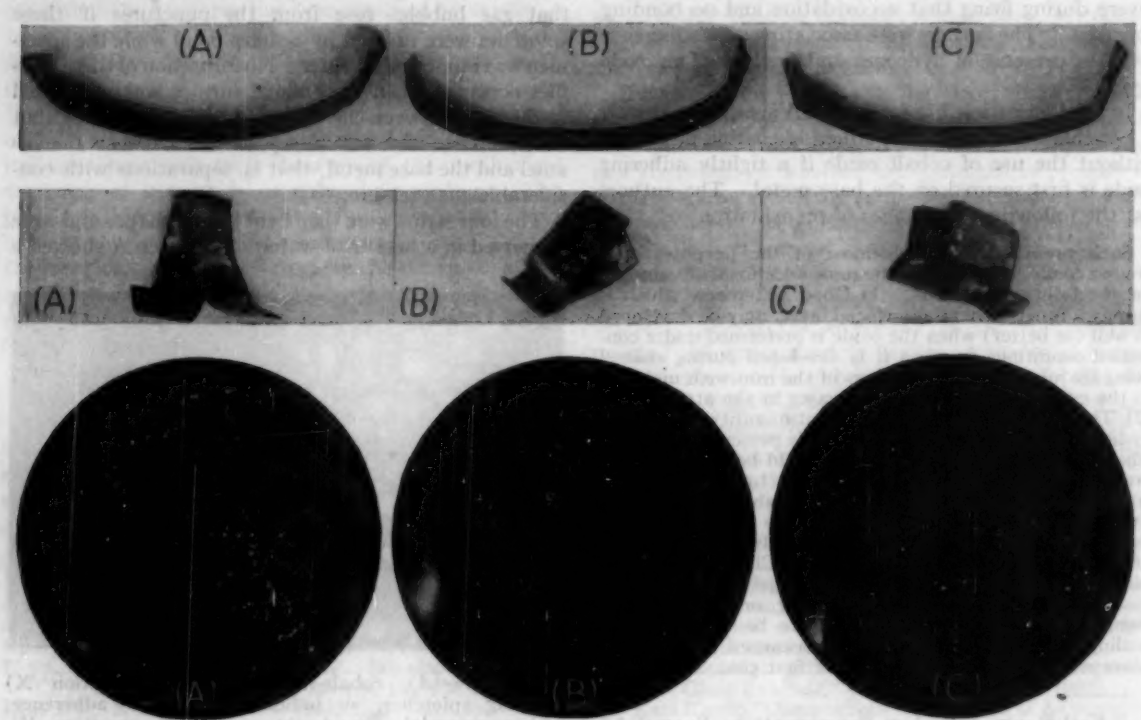

FIG. 3.—(*A*) cobalt-free enamel on iron; (*B*) cobalt enamel on iron; and (*C*) cobalt-free enamel on copper

the entrapped bubbles, was then photographed. The collected gas samples from the three specimens are shown at the bottom of Fig. 3. Specimen A, which consisted of enameling iron coated with cobalt-free ground coat, gave off much more gas than specimen B, which was the evolution from an iron sample coated with an ordinary commercial ground-coat enamel. Specimen C was copper, enameled with cobalt-free enamel, and gave off no gas whatsoever. All three specimens had a pronounced bubble structure in the glass coating, and the fact that the copper specimen gave off no visible quantity of gas was sufficient proof that the gas which collected under the watch glass was not gas from the bubbles in the glass itself.

Other pieces, similar to specimen A, were prepared, and the gas that was given off when the enamel coating was broken was collected over mercury. The gas sample was analyzed with a precision Burrell gas analyzer for oxygen, carbon dioxide, carbon monoxide, and hydrogen. The gas sample was found to be pure hydrogen.

(2) Relative Adherence of Enamel to Austenite and Ferrite

Zapffe and Faust[15] state that hydrogen is generally more soluble in metals having a face-centered cubic structure than in those having a body-centered cubic structure. Austenite, being face-centered cubic, should therefore dissolve more hydrogen at the same temperature than ferrite, which is body-centered cubic.

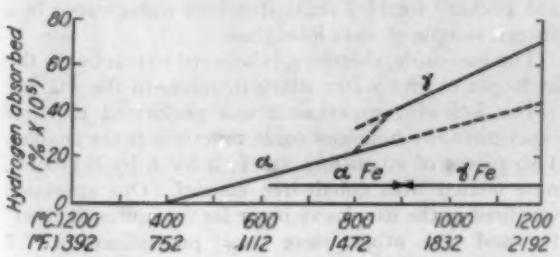

FIG. 4.—Diagram, slightly idealized, showing variation of reversible solubility with temperature for hydrogen in iron under 1 atm. of pressure[6]; iron-hydrogen, $K = (H)/\sqrt{pH_2}$.

Zapffe and Sims[6] showed that hydrogen was considerably more soluble at all temperatures in austenite than in ferrite. As may be seen in Fig. 4, the solubility of hydrogen in steel drops off sharply at the gamma-alpha transformation. It was thought, then, that austenitic stainless steel could be enameled more readily than ordinary enameling iron if this hydrogen theory were true. To check this reasoning experimentally, a plate of 16-gauge, 18–8 austenitic stainless steel, 4 by $1^1/_2$ in. in size, and a plate of 16-gauge enameling iron, 4 by $1^1/_2$ in. in size, were enameled and fired together in air. These pieces were enameled on both sides and

[15] C. A. Zapffe and C. L. Faust, "Metallurgical Aspects of Hydrogen in Electroplating," *Proc. Educational Sessions, Amer. Electroplaters Soc.*, **28**, 1–25 (1940).

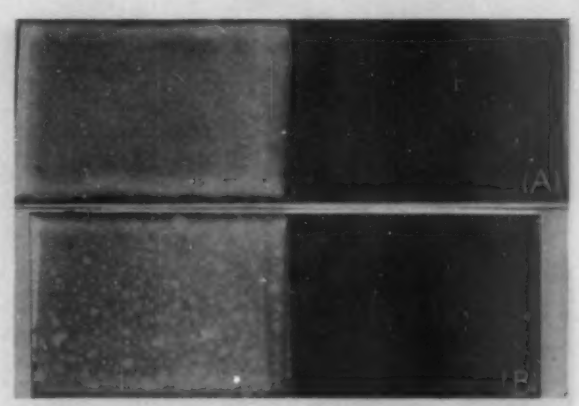

FIG. 5.—(*A*) 18–8 type stainless steel enameled with cobalt-free enamel at left and cobalt enamel, right; note freedom from splotches; (*B*) enameling iron coated with cobalt-free enamel at left and cobalt enamel at right; note splotched area at left, sign of poor adherence.

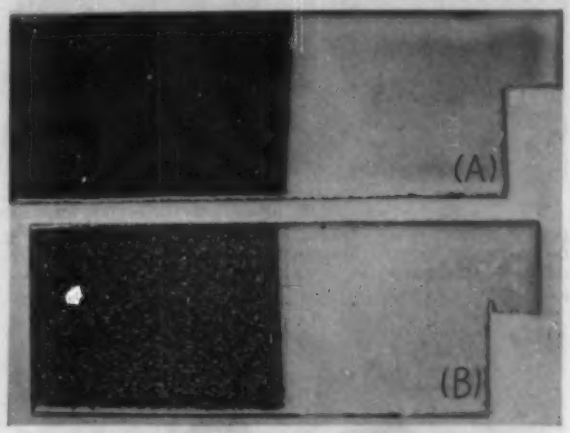

FIG. 6.—Same specimens shown in Fig. 5 after tests for reboiling tendencies; note many reboil blisters on enameling iron sample (lower), whereas (*A*), the 18–8 stainless steel sample is entirely devoid of this condition; (*B, right*) cobalt-free enamel shows very few reboil bubbles, an indication that reboiling is in some way related to the adherence oxides.

one half of each piece was coated with a regular commercial ground coat (enamel Y); the remainder of the piece was coated with essentially the same enamel except that no cobalt, nickel, or manganese oxide had been added at the smelter (enamel X) (see Fig. 5). The commercial ground-coat enamel gave a satisfactory coating on both pieces, but the cobalt-free enamel showed the characteristic splotchy appearance on the enameling iron. This splotchy condition was entirely absent on the 18–8 specimen, and the cobalt-free enamel appeared to adhere as satisfactorily as the cobalt ground coat to the stainless steel.

The plates shown in Fig. 5 were placed for 30 seconds in an enameling furnace at 1600°F. This is the customary test for reboiling, and the number of raised blisters in the enamel coating is a measure of the reboiling tendency. Figure 6 shows the appearance of the plates after the reboil test. The commercial ground-coat enamel reboiled severely on iron but not on

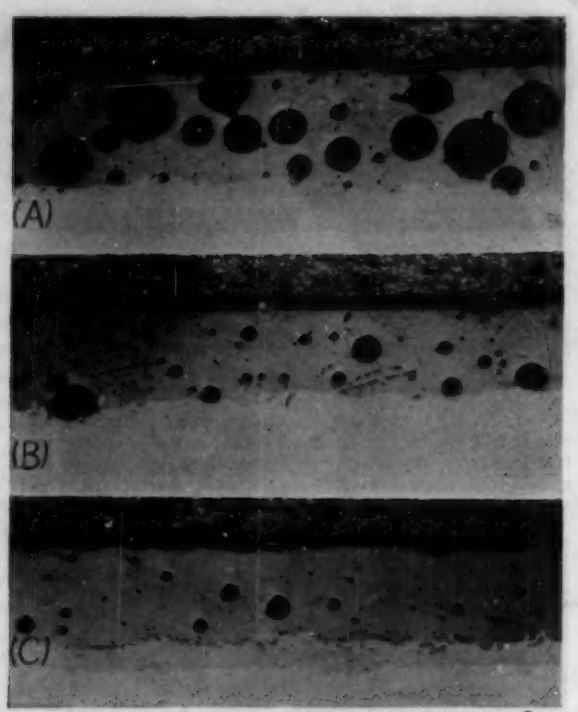

FIG. 7.—Photomicrographs of sections through enameled plates subjected to varying amounts of oxidation before firing in an inert atmosphere; (*A*) no oxidation; (*B*) oxidized 10 minutes at 1000°F.; (*C*) oxidized 20 minutes at 1100°F.; ×100.

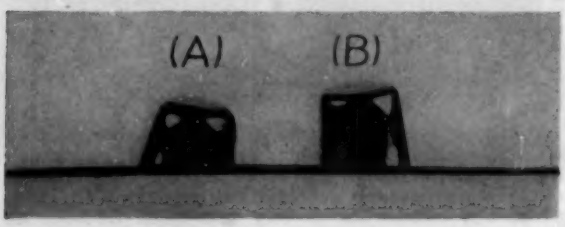

FIG. 8.—Beads from enamel frit showing comparative fusibility; (*A*) commercial ground coat; (*B*) same frit to which 10% of iron oxide has been added.

the stainless steel. The cobalt-free enamel reboiled slightly on the iron but not on the stainless steel. Here again is an example of the relationship between adherence and the reboiling phenomenon.

There is a different adherence behavior of enamel to 18-8 stainless steel and to enameling iron as well as a decided difference in the reboiling characteristics of the two metals. The reboiling and adherence behavior of enamel to these two base metals is readily explainable on the basis of the relative amounts of hydrogen which these metals can hold in solution at any given temperature.

(3) Role of Iron Oxide

The writer has mentioned in section II that an iron oxide layer at the interface was associated with good adherence because this layer prevents a hydrogen concentration at the iron-enamel contact zone. The reaction, $Fe + H_2O \rightarrow FeO + H_2$, which produces ferrous oxide from iron and water, tends to proceed to the right, provided there is an excess of iron and water and little or no iron oxide and hydrogen. When a considerable amount of ferrous oxide is present at the interface however, the reaction tends to proceed to the left and thus prevents the formation of hydrogen by the dissociation of moisture in the enamel and in the furnace atmosphere.

The oxidation of hydrogen by the iron oxide has the tendency to eliminate bubbles in the enamel formed during the firing period, and ferrous oxide therefore behaves as a fining agent (Fig. 7). This fining action of ferrous oxide was previously thought to be the result of its fluxing action on the glass.[16] It has been found, however, that glass containing 10% of iron oxide is more refractory than that which contains none, although 10% of this oxide is sufficient to decrease materially the bubble structure of the glass. In Fig. 8, (*A*) shows beads made from ground-coat frit powder and (*B*), beads made from this same powder with a 10% ferrous oxide addition. These beads were fused at 1400°F. for 5 minutes and, as may be seen, the enamel containing the iron oxide is the more refractory. Because the iron oxide does not act as a fluxing agent, the only manner in which it could fine out the gas bubbles in the glass would be to react with the gas to produce an end product which was not a gas or else was a gas soluble in the glass itself. Water vapor is one of the very few gases which is soluble in glass.[8] Salmang and Becker[17] found 5 cc. of dissolved water vapor in a 10-gm. sample of soda-lime glass.

The iron oxide, therefore, is believed to react with the hydrogen to give water which dissolves in the enamel.

The following experiment was performed to show experimentally how iron oxide functions in the enamel. Two pieces of enameling stock, 3 by 6 by 0.110 in., were coated with cobalt-free enamel. One specimen was fired in the usual way in air for 9 minutes at 1600°F., and the other piece was preoxidized for 7 minutes at 1050°F. and was then transferred to a furnace at 1600°F. where it was fired for 9 minutes in a neutral (slightly oxidizing to iron) atmosphere. After cooling to room temperature, the pieces appeared as shown in Fig. 9 (*A*, *a*). The specimen at the left, which had been fired in air, was covered with splotches and fish scales, but the specimen at the right was free from these blemishes. Microscopic examination of the enamel surface of the specimens showed that both pieces appeared to have similar extensive bubble structures (see Fig. 9 (*B*,*b*)). On the basis of past research[18] during which it was found that a large and extensive bubble structure prevented fish scaling, the difference

[16] W. W. Higgins and W. A. Deringer, "Investigation of Fish-Scale Phenomena," *Jour. Amer. Ceram. Soc.*, **24** [12] 383-92 (1941).

[17] A. Becker and H. Salmang, "Gases in Glass: II, Gas and Moisture Content of Glasses," *Glastech. Ber.*, **6** [11] 625-34 (1929); *Ceram. Abs.*, **8** [9] 643-44 (1929); for English translation of entire paper, see *Jour. Soc. Glass Tech.*, **13** [49] 98-111 (1929).

See also footnote 8.

a wonderful picture

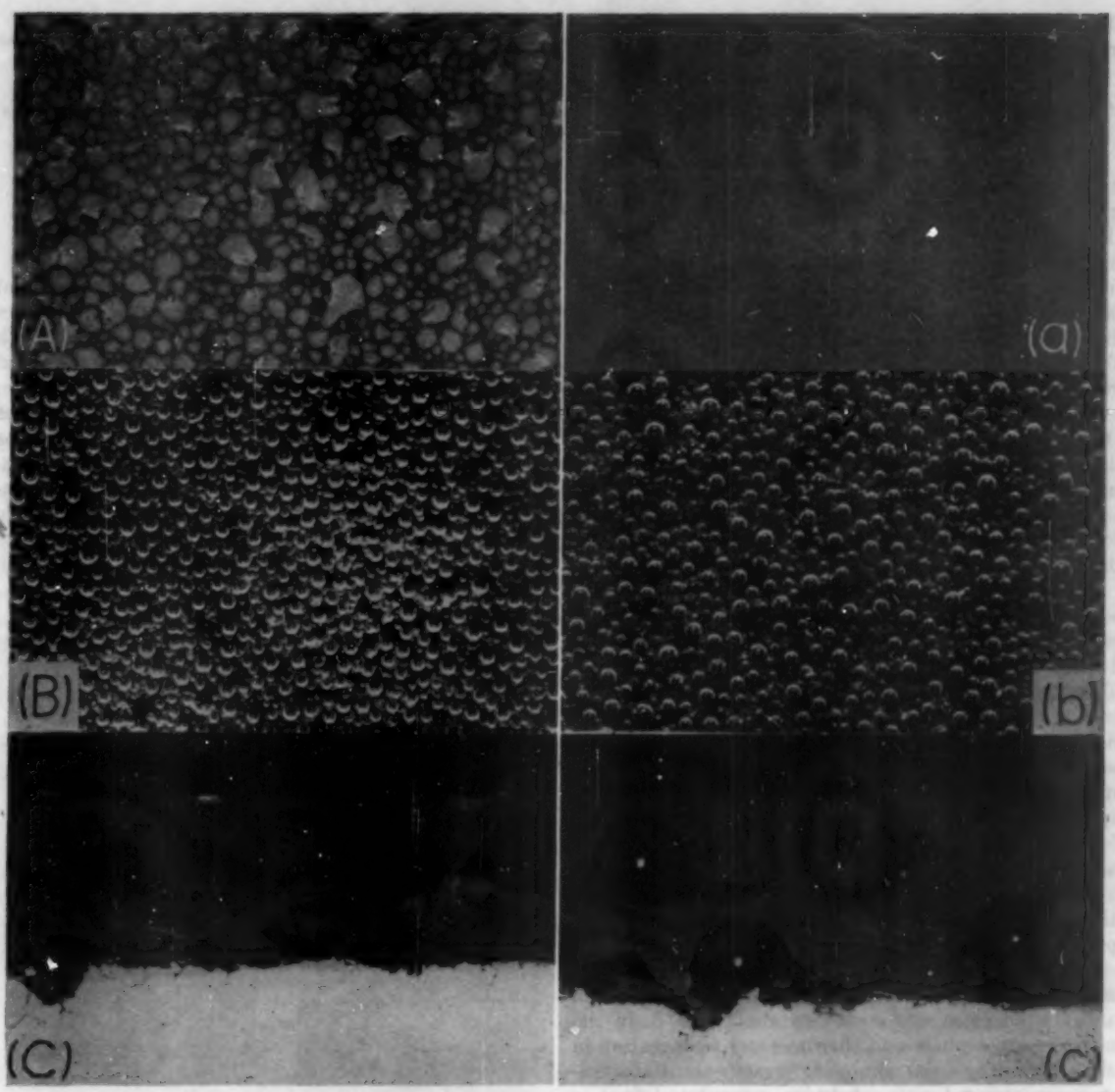

FIG. 9.—Effect of furnace atmosphere (which directly affects amount of oxidation of base metal) on appearance and structure of cobalt-free ground-coat enamel; *left*, specimens fired in air; *right*, specimens fired in controlled atmosphere; (*A*,*a*) comparative appearance of specimens, actual size; (*B*,*b*) bubble structure of specimens using oblique lighting, ×30; (*C*,*c*) photomicrographs through enamel coating showing bubble structure; note absence of bubbles at interface in specimen at left (*C*), ×200.

in behavior of the two specimens was difficult to explain.

Microsections through the metal-enamel interface, however, revealed the cause for this difference of behavior. The photomicrograph of the specimen fired in air (Fig. 9 (*C*)) showed the glass to be remarkably free from bubbles at the interface although this enamel had an extensive bubble structure. Thus there were no bubbles in which the hydrogen could accumulate, and the resultant gas pressure caused the separations at the interface (splotches) and exploded the enamel away from the base metal in many places (fish scales). The photomicrograph of the specimen fired in a controlled atmosphere (Fig. 9 (*c*)) showed that an extensive bubble structure extended to the base metal and prevented a build-up of gas pressure at the interface.

The base metal of the specimen fired in air received considerably more oxidation than that fired in a controlled atmosphere, and this oxide served to fine the glass free of bubbles at the metal-enamel interface.

The freedom from defects of the piece fired in a controlled atmosphere was no indication that the adherence was satisfactory as was demonstrated by flexing the specimens shown in Fig. 9 (*A*,*a*). The adherence of both pieces was very poor, indicating the presence of hydrogen at the interface of both pieces. The difference in behavior of the two coatings was caused not by the presence of hydrogen at one interface and not at

the other but by a difference in gas pressure at the two interfaces.

(4) Effect of Varying Quantities of Hydrogen on Adherence

Enameling iron specimens, containing little or no hydrogen, an intermediate amount of hydrogen, and much hydrogen, were prepared on the theory that this experiment would contribute worth-while information on adherence. Thin-gauge pieces were chosen for this work because (1) with very thin gauges, a larger proportion of the hydrogen in the metal may be expelled than is possible on heavier gauges[3(a)]; (2) a thin piece of steel will not take up as much hydrogen from the clay and water in the enamel during firing as a heavier piece because less gas is required to saturate the base metal than with heavier gauges; and (3) a light-gauge specimen may be flexed readily to determine how well the enamel adheres to it.

Four specimens, $2^1/_2$ by $1^3/_4$ by 0.018 in., were used for this test. These specimens are listed in order of decreasing hydrogen content.

Specimen E was prepared by cleaning in a boiling solution of an alkaline cleaner, the concentration of which was 6 ounces to the gallon; it was then pickled for 15 minutes in a 7% sulfuric acid solution at 145°F. The specimen was rinsed in cold water and neutralized in a 0.2% sodium cyanide solution for 30 seconds. The neutralizer was heated only to 160°F. so as not to drive off much of the dissolved hydrogen taken up by the metal during the pickling operation. This piece was sprayed with cobalt-free enamel, dried in front of a fan without the application of any heat, and fired in air for 2 minutes at 1600°F.

Specimen F was prepared by sandblasting; it was then sprayed with cobalt-free enamel, dried over a hot plate, and fired at 1600°F. for 2 minutes.

Specimen G was annealed five times in an atmosphere of dry (oil-pumped) nitrogen at 1600°F.; after each anneal, the piece was cooled to about 300°F. in the nitrogen atmosphere and then to room temperature in air. Following these annealing treatments, the specimen was sprayed with cobalt-free enamel and fired in air for 2 minutes at 1600°F.

Specimen H was given the same annealing treatment as specimen G. After sandblasting, this piece was dipped in a slip prepared by mixing dry ground frit of cobalt-free enamel with ethyl alcohol in a mortar and was dried for 30 minutes at 400°F. to remove all possible moisture and to evaporate the alcohol. The specimen was then fused in an atmosphere of dry nitrogen for 2 minutes at 1600°F.

Table II shows the various sources of hydrogen present in enameled specimens E, F, G, and H. It is assumed that the initial hydrogen present in the metal of specimens G and H was removed by the annealing treatment, although a small residual portion of this gas may not have been driven off by this means.

Figure 10 shows the appearance of these specimens after enameling. Specimen E is entirely devoid of enamel because, after cooling, the enamel exploded from the base metal, leaving the shiny metal surface shown in the picture. The enamel adheres to the base metal of specimen F, but the splotchy appearance indicates poor adherence and gas pressure at the interface. Both specimens, G and H, have good gloss and texture and better adherence than specimens E and F. Specimen H is quite glossy and almost entirely devoid of bubbles in spite of the fact that the enamel was fused to the metal (without preoxidation) in a dry nitrogen atmosphere. This piece shows that when the hydrogen content is kept low enough to cause no harm, an oxide layer at the interface is unnecessary nor is it necessary to have a bubble structure in the glass to prevent fish scaling.[18]

TABLE II

Specimen	Initial hydrogen in base metal	Sources of hydrogen: From pickling	From clay and water in enamel	From furnace atmosphere
E	X	X	X	X
F	X		X	X
G			X	X
H				

X denotes presence of gas from source indicated.

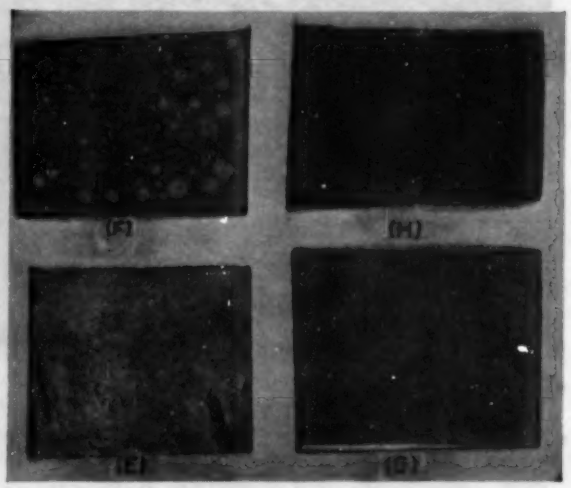

FIG. 10.—Fired specimens listed in Table II; (*E*) entirely devoid of enamel; (*F*) splotchy condition indicates poor adherence; (*G*) and (*H*) fair adherence; (*H*) is darker in color than (*G*) because it is free from bubbles.

(5) Relation of Stock Thickness to Adherence of Cobalt-Free Enamel

It has just been mentioned that thin stock cannot take up or dissolve as much hydrogen as thicker sections. The reason is obvious, but the effect of this difference in hydrogen absorption is shown in Fig. 11. Specimens J and K were 0.018-in. enameling stock and specimen L was 0.050-in. enameling stock. Specimens K and L were coated with cobalt-free enamel, and specimen J was coated with a typical commercial ground coat. The coatings of all three specimens were fractured by impressing a 1-in. ball bearing into the surface of each specimen, making a depression in each piece about $^1/_4$ in. deep. The adherence of the enamel of

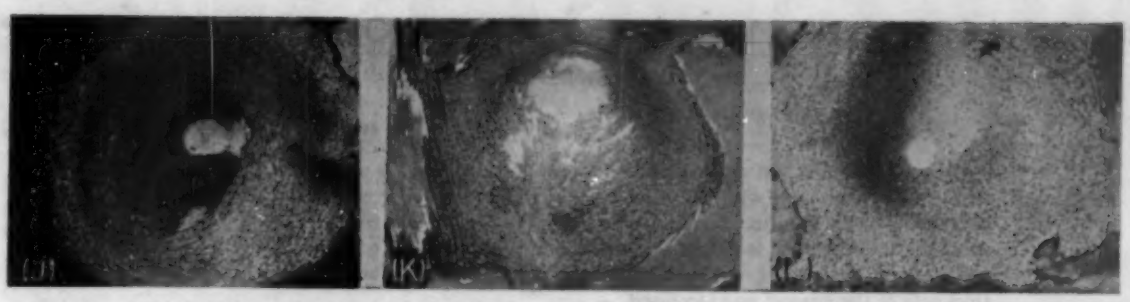

FIG. 11.—(*J*) 0.018-in. stock enameled with cobalt ground coat (composition Y); (*K*) 0.018-in. stock enameled with cobalt-free ground coat (composition X); (*L*) 0.050-in. stock enameled with composition X; each sample has been fractured with a 1-in. steel ball by forming cup 1/4 in. deep in specimens; amount of fragmented glass adhering to base metal is measure of adherence of glass to metal; fractures in (*J*) and (*K*) indicate good adherence, whereas that of (*L*) is poor.

specimen K was almost as good as specimen J; but the glass broke away quite cleanly from the base metal of specimen L, leaving but slight evidence of the tiny adhering particles of glass which characterize the fractures of specimens J and K. This illustration demonstrates that the need for cobalt oxide in the enamel to promote adherence is not nearly so great for thin gauges (where the amount of hydrogen present is less) as for heavier gauges of enameling iron. The gauge of the stock obviously has an important bearing on fish-scaling and reboiling tendencies as well,[18] which constitutes further proof that a relationship exists between adherence, reboiling, and fish-scaling phenomena.

V. Summary

The references cited from the literature and the experimental data corroborate and justify the theory advanced at the beginning of this investigation. According to this theory, porcelain enamel requires no intermediate layer at the interface to promote adherence to iron, and, were it not for the presence of hydrogen in the base metal, enamel would adhere as readily to iron as to copper, gold, or silver. Even if the enameling of iron itself is alloyed with other elements so as to give austenite at room temperature and thereby to increase hydrogen solubility, the difficulties encountered in obtaining good adherence are decreased.

The presence of hydrogen in the base metal, however, together with the tremendous decrease of solubility of this gas while cooling to room temperature combine to create a hydrogen gas layer at the interface which prevents satisfactory adherence. It has been shown that, to get satisfactory adherence, some substance must be introduced into the enamel (such as cobalt oxide or nickel oxide) or else hydrogen must be eliminated entirely from the system. Poor adherence has been shown to be associated with gas pressure at the interface, whereas when good adherence is obtained, the gas present between the base metal and the enamel is very low. The shiny surface of the base metal, when the adherence is poor, is further evidence that some reducing agent has been at work at the interface. There is considerable evidence in the literature to show that reboiling and fish-scaling phenomena are caused primarily by hydrogen; and the relationship shown in this investigation between adherence, reboiling, and fish scaling is further proof (albeit indirect) that adherence of porcelain enamel to enameling iron depends to a great extent on the amount and nature of hydrogen present. Some oxidizing agent, such as ferrous oxide, is necessary to oxidize the hydrogen in order to counteract the hydrogen at the interface. It is in this connection that cobalt oxide probably plays its part. The cobalt oxide may serve as an oxygen carrier to maintain an iron oxide layer at the interface, which in turn reacts with the hydrogen content to give water. It is only when no hydrogen is present in the base metal and when none is introduced during the enameling process that good adherence can be obtained without cobalt oxide and nickel oxide in the enamel.

A possible explanation of the presence of isolated dendrites of alpha iron in the glass is that a portion of the ferrous oxide which has penetrated the glass layer (through solution in the glass) is reduced by hydrogen from the chemically combined water and organic matter in the clay to give isolated particles of iron. The oxide layer itself is never in equilibrium, and the reduction of part of this iron oxide by hydrogen may yield the isolated particles of alpha iron in the interface which have been identified as dendrites by several investigators.[3,4] On the basis of this explanation, there would be an indirect connection between adherence and the presence of dendrites at the interface.

To make the explanation complete, it is necessary to account for the water formed in the reaction, $FeO + H_2 \rightarrow Fe + H_2O$. A possible explanation may be the high solubility of water vapor in glass.[17] The water vapor going into solution would leave no bubbles, a condition which exists in the enamel layer when there has been substantial oxidation of the base metal.

Acknowledgment

The writer wishes to express his gratitude to the management of the A. O. Smith Corporation of Milwaukee, Wis., for their permission to use the facilities of the Ceramic Research Laboratory in connection with this investigation. He is also grateful to W. W. Higgins, director of ceramic research at the A. O. Smith Corporation, for his assistance and cooperation in this research problem.

A. O. SMITH CORPORATION
MILWAUKEE, WISCONSIN

[18] A. I. Andrews and R. E. Mullady, "Further Data on Reboiling," *Jour. Amer. Ceram. Soc.*, **17** [11] 346–48 (1934).

RELATION OF THICKNESS TO IMPACT RESISTANCE OF PORCELAIN ENAMEL*

By Roger L. Fellows

Abstract

Chipping of porcelain enamel on the flanges of table tops as a result of impact was studied and compared with the results obtained from the Porcelain Enamel Institute tentative standard impact test. A correlation was found to exist between the results using the P.E.I. test on standard 1-in. tubes and those obtained on the corner of a table-top flange. The impact resistance of enamels applied over a radius also increased as the thickness of the enamel was increased.

I. Introduction

An enamel shop making table tops changed from the use of an opaque enamel to a superopaque, antimony-free enamel to reduce the enamel thickness. The latter enamel was found to chip more easily than the opaque, antimony-bearing type when the corner of the flange was struck with a wooden mallet. This seemed to be a crude test, but it had been used quite successfully in checking the chipping resistance of this type of ware.

An investigation was undertaken to determine by a more scientific means the difference in impact resistance of the two enamels involved and whether this difference was due to the type of frit used or to the varying thicknesses of the enamel.

In this work, it must be remembered that the chipping of the enamels that were tested was the result of impact on a radius and should not be confused with chipping from other causes, such as bending in tension or compression, twisting, or spontaneous chipping. The different types of chipping have been previously described.[1]

II. Test Procedures and Results

The impact tests were made on three types of specimen, namely, table tops, sections of table-top flanges, and standard 1-in. cylinders, 9 in. long as specified in the tentative standard impact test of the Porcelain Enamel Institute.[2]

(1) Table Tops

The table tops on which the impact tests were made were enameled in ground coat in the usual manner; one half was dipped in an opaque, nonacid-resisting, cover-coat enamel, A, for the first coat. The other half was dipped in an antimony-free superopaque enamel, B. A lighter weight of application of the B enamel was used because of its superior covering power. All of the tops were finished in second coat by dipping in an acid-resisting enamel, C. Two representative tops from each group were selected, and the thickness of the enamel coating was determined through a cross section of the flange with the aid of a microscope. The total thickness of enamel on the table tops using cover coat A was 0.0168 in. and on the top using cover coat B was 0.0138 in.

An accessory piece of equipment was attached to the P.E.I. impact test apparatus so that tests could be made on the corner of the flange of the table tops. The accessory piece shown in Fig. 1 consisted of an anvil designed to support the flange with no support directly behind the apex to be tested. Thirty-six spots about $1^1/_2$ in. apart were tested on each of two table tops of each type. This made a total of 72 spots tested on the two tops, which is the same number used on 6 standard cylindrical specimens in the P. E. I. test.

The results are tabulated in Table I.

Table I

Enamel first coat*	Total enamel thickness (in.)	Avg. failure	
		No. of blows	Ft.-lb.
A (opaque)	0.0168	4.0	0.050
B (superopaque)	0.0138	2.4	0.030

* Second coat, enamel C, acid resistant.

These results confirm those of the practical shop tests in that the tops with the opaque enamel at a

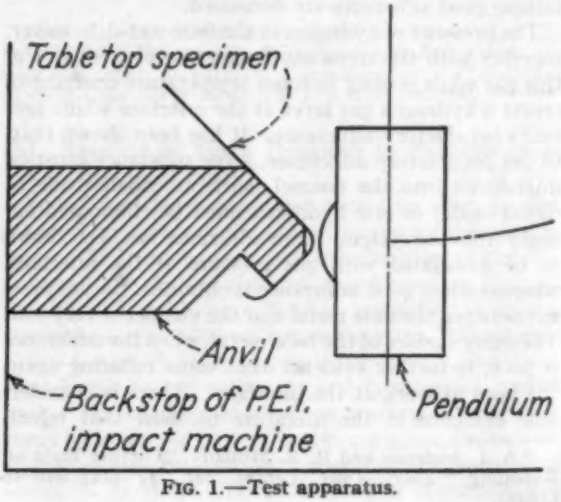

Fig. 1.—Test apparatus.

* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, April 20, 1943, Pittsburgh, Pa. (Enamel Division). Received January 2, 1943.

[1] P. L. Smith, "Chipping Resistance of Enamels," pp. 155–62, *Proc. Porcelain Enamel Inst. Forum, Fourth Forum, Oct., 1939; Ceram Abs.*, 19 [7] 156 (1940).

[2] "Impact Test for Laboratory Specimens of Porcelain Enamel Sheet Iron and Steel," *Porcelain Enamel Institute Tentative Standard Bull.*, August, 1940; for an abstract of this test, see P. L. Smith, "Development of Two Tentative Standard Tests," pp. 130–33, *Proc. Porcelain Enamel Inst. Forum, Fifth Forum, Oct., 1940; Ceram. Abs.*, 20 [4] 85 (1941).

thickness of 0.0168 in. had a better impact resistance on the radius of the flange than the tops enameled with the superopaque enamel, 0.0138 in. thick.

(2) Sections of Table-Top Flanges

For an additional check on these results under laboratory conditions, in which the weights of application of the enameled specimens could be carefully controlled, 12-in. sections of the flange were made with the same die that was used in forming the table tops (Fig. 2).

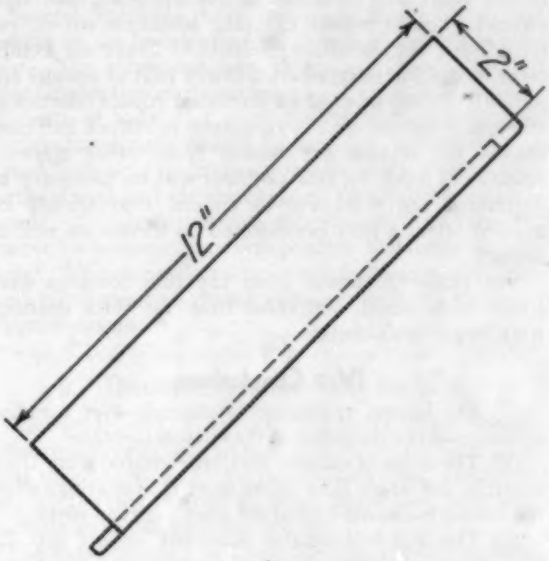

FIG. 2.—Section of table-top flange.

The 12-in. sections were dipped in a commercial ground-coat enamel, applying 0.004 to 0.005 in. of ground coat on the corners of the flange as measured with a Brenner magnetic thickness gauge. Nine of the specimens were enameled in first-coat white with an average of 0.0069 in. of opaque enamel A, nine with 0.0063 in. of superopaque enamel B, and nine with 0.0093 in. of enamel A. All were finished in second coat with 0.005 in. of acid-resisting enamel C. Each enamel was applied by dipping and draining, and all measurements were taken on the corner of the flange with a Brenner magnetic gauge. Impact tests were made on the corner of the flange with the specimen held in position over the special anvil. Eight spots were tested along the edge of each of the nine specimens. The results are tabulated in Table II.

TABLE II

Enamel first coat*	Total enamel thickness (in.)	Avg. failure	
		No. of blows	Ft.-lb.
A (opaque)	0.0165	6.18±0.33	0.077±0.004
B (superopaque)	0.0160	6.30±0.39	0.079±0.005
A (opaque)	0.0195	7.40±0.44	0.092±0.005

* Second coat, enamel C, acid resistant.

The statistical error was determined for the tests of the nine specimens, assuming a percentage confidence of 95 as outlined in the P.E.I. tentative standard test.

TABLE III

PERCENTAGE CONFIDENCE OF DIFFERENCE IN GROUPS OF SPECIMENS

Enamel	Thickness (in.)	Confidence (%)
A C	0.0165	Below 90
B C	.0160	
A C	.0165	99
A C	.0195	
B C	.0160	99
A C	.0195	

The basis of classification for percentage confidence figures as recommended by the P.E.I. test is as follows:

99% or higher, highly significant
95–99%, significant
90–95%, indicative
Below 90%, not recommended for consideration

The statistical treatment of the data shows that there is no difference in the impact resistance of the specimens enameled with enamels A or B but that there is a significant improvement of the impact resistance when the thickness of the enamel was increased.

(3) Standard 1-In. Cylinders

Inasmuch as the foregoing tests of table-top specimens showed that the impact resistance on a curved surface increased as the thickness of the enamel increased, additional tests were made by using the P.E.I. standard impact test of 1-in. cylindrical specimens. Standard cylinders, 1 in. in diameter by 9 in. long, were enameled in ground coat, 0.003 ± 0.0003 in. thick. One, two, or three coats of antimony-free, superopaque, white cover coat were then applied to obtain a total enamel thickness (ground coat plus cover coat) of approximately 10, 15, 20, and 25 mils. The specimens were tested according to the P.E.I. tentative standard impact test. Results are shown in Table IV.

TABLE IV

Specimen No.	Total enamel thickness (in.)	Avg. failure	
		No. of blows	Ft.-lb.
1	0.0103±0.0005	8.80±0.46	0.110±0.006
2	.0157±0.0005	9.12±0.42	.114±0.005
3	.0215±0.0005	9.62±0.37	.120±0.005
4	.0252±0.0005	10.82±0.61	.135±0.008

TABLE V

Specimen No.	Confidence (%)
1, 2	Below 90
1, 3	98.5
1, 4	99.5
2, 3	92
2, 4	99.8
3, 4	99.2

The percentage of confidence that a systematic difference exists between results of these specimens is shown in Table V.

The results show definitely that the impact resistance of an enamel over a radius is improved by an increase in the thickness of the enamel. A curve of these results is shown in Fig. 3.

III. Results

This investigation indicates that the method of testing 1-in. cylinders by the P.E.I. tentative standard test gives results comparable to those obtained over a radius of a flange as tested on laboratory specimens as well as on parts enameled under production conditions. Although the reason for greater impact resistance of one enamel over another was not shown by crude shop test methods, the tentative standard impact test method revealed that the difference was a result of the thickness of the enamel rather than of the type of enamels involved.

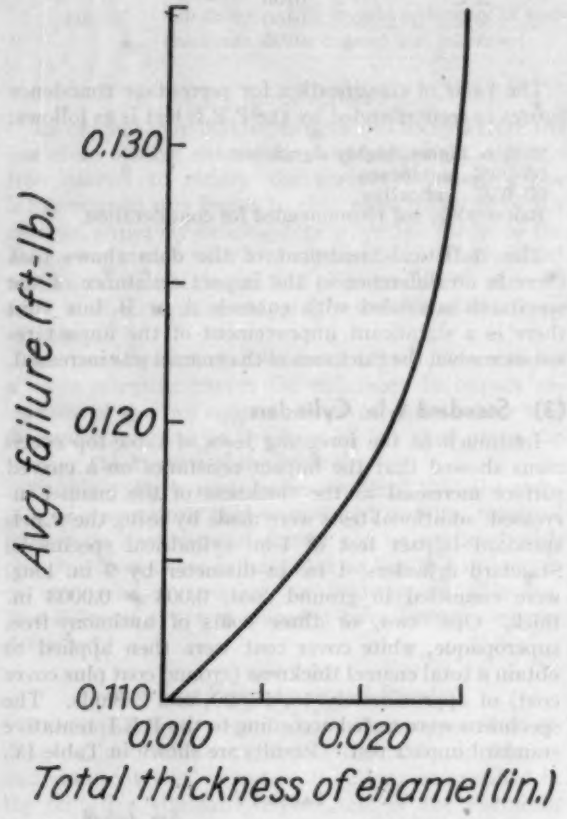

FIG. 3.—Relation of total thickness of enamel to resistance to impact.

The present investigation indicates that the impact resistance of enamel over a radius increases as the enamel thickness increases. Thick enamel coatings, however, are not a solution of the chipping problem. In the introduction of this paper, chipping of porcelain enamel was shown to occur from other causes than impact failure. The experience of the industry during recent years has produced ample evidence that thin enamel coatings reduce chipping losses on stoves, refrigerators, and similar products.[3] There are conditions in this industry where a heavy coat of enamel apparently should be used for increased impact resistance, whereas a lighter coat is necessary to reduce chipping caused by strains or stresses from other sources. Additional work on this problem will be necessary to determine the thickness of enamel that should be applied when a part is subjected to torsion as well as impact.

The chips of enamel from the thin coatings were found to be small, and those from the thick coatings were larger in diameter.

IV. Conclusions

(1) The impact resistance of enamels over a radius increases as the thickness of the enamel increases.

(2) The chips of enamel that are removed from thick coatings are larger than those from thin coatings when the failure is caused by impact over a curved surface.

(3) The P.E.I. tentative standard impact test for laboratory specimens of porcelain enameled sheet iron and steel requires the use of a 1-in. cylinder test specimen, and this work shows that a correlation exists between the results secured with the P.E.I. test and those on rigid curved surfaces.

LUSTERLITE LABORATORIES
CHICAGO VITREOUS ENAMEL PRODUCT COMPANY
CICERO, ILLINOIS

[3] H. H. Helscher, "Measurement and Significance of Enamel Thickness," *Jour. Amer. Ceram. Soc.*, **19** [10] 298–303 (1936).

SIMPLIFIED THERMAL-EXPANSION RINGS FOR PRODUCTION CONTROL IN TERRA COTTA MANUFACTURE*

By T. E. Nicholson and Fred L. Goin

Abstract

An improved and simplified method of manufacturing rings for determining glaze stresses has been developed, which gives reliable results without excessive laboratory expense.

I. Introduction

Several methods have been employed to detect strains set up by unbalanced glaze and body relationship. The more common of these methods are (1) visual inspection of glazed ware for crazing or shivering; (2) tests of body and glaze by quenching at various temperatures until failure occurs; (3) autoclaving of glazed bodies[1]; (4) shrinkage test in which a cylinder is partly glazed and the shrinkage of the glazed portion is noted[2]; (5) curvature of a glazed bar[3]; (6) interferometer to measure the average glaze and body expansions[4]; (7) polarization microscope to measure thin sections cut normal to glazed surface[4]; and (8) thermal-expansion rings.

II. Thermal-Expansion Rings for Tests

Schurecht and Pole[5] developed a 2-in. hollow cylindrical ring glazed on the outside for the measurement of glaze stress. Davis and Lueders[6] sought to simplify the ring method by using rings, 3 in. in outside diameter with the addition of a lug.

The hand pressing of these rings is a tedious, time-consuming procedure. By converting a hand-cranked meat grinder into a ring-extrusion apparatus and adding certain simplifications in measurement, the writers found that the use of glaze-stress ring tests could be greatly facilitated.[7]

III. Extruded Rings

Figure 1 shows the converted meat grinder. The tempered body is fed into the hopper and forced by the auger through a shredder which lessens the characteristic weaving of the single-wing auger. The spaghetti-like columns of the shredded body are compressed together by the die into a cylindrical column, 4 in. in outside diameter, $^1/_4$ in. in wall thickness, and having a lug $^1/_2$ in. wide. The column is extruded onto a mandrel and cut off at the die face. A plaster mold is clapped around the mandrel-supported ring, and the nibs are pressed in the lug. After trimming to size, the mandrel is removed and the ring is dried (Fig. 2). A dozen plaster molds are sufficient for continuous operation.

IV. Glazing of Rings

The dried rings are racked and sprayed on a revolving easel; these rings may be stacked ten high with little danger of the bottom ring breaking. By spraying a measured quantity of glaze on the racked rings and checking with a micrometer thickness gauge, fairly uniform glaze thicknesses are obtained. Inasmuch as the viscosity of the molten terra-cotta glazes permit heavy application without excessive running, the error resulting from the varying glaze thickness is lessened by spraying to a thickness of 0.025 in.

V. Measurement of Rings

Davis and Lueders[6] have advocated the use of viscous glaze beads as reference points on opposite ends of a $^1/_2$-in. lug incorporated on the side of the expansion ring. These beads, which "fuse to a rather perfect hemisphere, approximately $^1/_{16}$ in. in diameter," were not easily established directly opposite each other nor

Fig. 1.—Converted meat grinder; (*a*) shredder plate and core assembly; (*b*) die; (*c*) mandrel for receiving rings from die; (*d*) plaster molds for pressing nibs in lug; and (*e*) racked rings showing reference nibs and $^1/_2$-in. lug.

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* Received May 11, 1942.

[1] H. G. Schurecht, "Methods for Testing Crazing of Glazes Caused by Increases in Size of Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **11** [5] 271–77 (1928).

[2] W. Steger, "Strain in Glazed Ware and Its Detection," *Ber. deut. keram. Ges.*, **9** [4] 203–15 (1928); *Ceram. Abs.*, **7** [9] 625 (1928).

[3] W. L. Shearer and W. R. Wyckoff, "Thermal Expansions of Whiteware Materials and Bodies Over a Wide Temperature," *Ceramist*, **7** [6] 349–85 (1926); *Ceram. Abs.*, **5** [7] 223 (1926).

[4] K. Litzow, "Tension Measurements of Glazed Ware by Polarization Microscope," *Sprechsaal*, **69** [21] 297–99 (1936); *Ceram. Abs.*, **15** [11] 339 (1936).

[5] H. G. Schurecht and G. R. Pole, "Method of Measuring Strains Between Glazes and Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **13** [6] 369–75 (1930); also in *Bur. Standards Jour. Research*, **5** [1] 97–103 (1930); R. P. 189.

[6] H. E. Davis and R. L. Lueders, "Simplification of Ring Method for Determining Glaze Stresses," *Jour. Amer. Ceram. Soc.*, **15** [1] 34–36 (1932).

[7] The reader is also advised to refer to the following papers: (*a*) A. M. Blakely, "Life History of a Glaze: II, Measurement of Stress in Cooling Glaze," *Jour. Amer. Ceram. Soc.*, **21** [7] 243–51 (1938); and (*b*) W. C. Bell, "Evaluation of Glaze-Fit Test Methods," *ibid.*, **23** [6] 163–66 (1940).

were they always perfect. The use of a small hemisphere, moreover, added certain errors of significant magnitude. The type of reference point made little difference when measurements were taken each time along the same reference line. In using the micrometer caliper, however, it was difficult to maintain the same reference line. This first measurement might be made normal to the *c* axis (Figs. 3 and 4) and the second at an angle of 9 degrees to the first or vice versa. Large nibs were adopted as reference points to minimize the errors resulting from variation in the line of measurement.

Equations shown in Figs. 3 and 4 demonstrate the superiority of large nibs over small; by substituting actual distances in these equations, only small errors in measurement occur.

$2R$ = 0.5000 in. (distance between points)
r = 0.0300 in. (radius of small nib)
r_1 = 0.2500 in. (radius of large nib)
$2m$ = 0.0600 in. (total contraction on cutting).

Substituting in the equation for percentage of error of Fig. 3,

$$\left[\frac{(0.2200 + 0.0300) - (0.2200 \cos 9° + 0.0300)}{(0.2200 + 0.0300)}\right] 100 =$$

1.1% (error in measurement).

Substituting in the equation for percentage of error of Fig. 4,

$$\frac{\frac{0.0600}{2}(\cos 9° - 1)(100)}{0.2500 - \frac{0.0600}{2}} = 0.17\% \text{ (error in measurement)}$$

These errors seem insignificant until they are translated into terms of movement caused by contraction, as shown by cases (1) and (2).

(*A*) *Case* (*1*): The measurement before cutting was made on an angle of 81 degrees to the axis, *cc'*, and the measurement after cutting was made normal to the axis.

Using large nibs as reference points (Fig. 4), the measurements were as follows:

	(In.)
Measurement before cutting	0.5000
" after "	0.4400
Recorded movement	0.600
Actual "	0.600
Error	None

Using small nibs as reference points (Fig. 3), the following measurements were obtained:

	(In.)
Measurement before cutting	0.4946
" after "	0.5400
Recorded movement	0.0546
Actual "	0.0600

Error $\frac{100(0.600 - 0.0546)}{0.0600} = 9\%$.

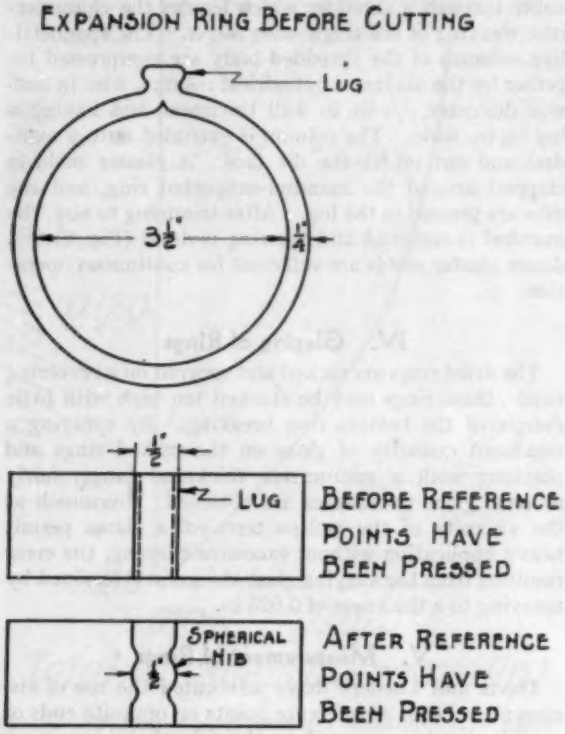

FIG. 2.—Plaster mold of test mandrel.

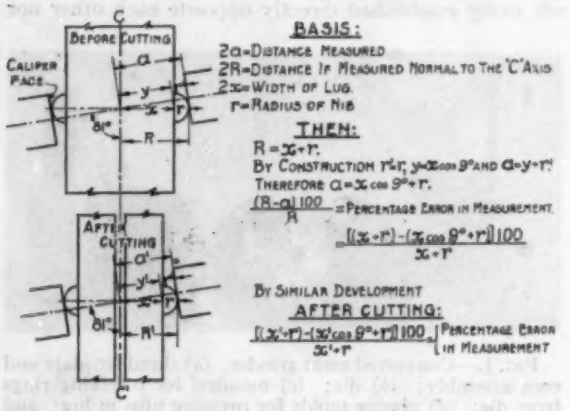

FIG. 3.—Use of small nibs as reference points.

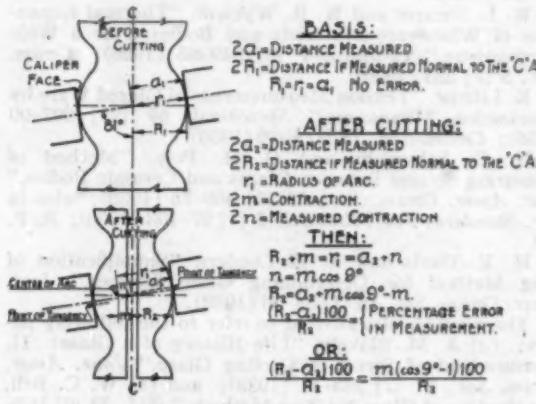

FIG. 4.—Use of large nibs as reference points.

(*B*) *Case* (*2*): The measurement before cutting was made normal to axis *cc'* and after cutting on an angle of 81 degrees to axis *cc'*.

Using large nibs as reference points (Fig. 4),

	(In.)
Measurement before cutting	0.5000
" after "	0.4404
Recorded movement	0.0596
Actual "	0.0600

$$\text{Error } \frac{100(0.0600 - 0.0596)}{0.0600} = 0.67\%.$$

Using small nibs as reference points (Fig. 3),

	(In.)
Measurement before cutting	0.5000
" after "	0.4352
Recorded movement	0.0648
Actual "	0.0600

$$\text{Error } \frac{100(0.0600 - 0.0648)}{0.0600} = -8\%.$$

The large pressed nib insures uniform location of the reference points and a smooth surface and also permits considerable latitude in the angle of measurement.

Actual measurement of rings featuring both types of reference points has verified the greater accuracy of the large nib.

The use of a micrometer caliper made necessary a method of holding the cut rings free from movement when the ratchet was tightened. Paraffin was first tried to hold the nibs in position, but it actually pulled them together when they were cooled. Dennison's sealing wax proved to impart practically no movement to the rings and was used in all subsequent tests. The wax was heated with a soldering iron and dropped on the ends of the lug; on cooling, the wax held the nibs rigidly in position for measurement.

After the rings had been measured for glaze stress, the wax was removed and the test pieces were subjected to autoclaving. The moisture expansion of the glaze and body was registered by a measurable movement of the rings. Thus by three measurements, that is, before cutting, after cutting, and after autoclaving, the stress relation between the glaze and body on drawing from the kiln and after moisture expansion was determined.

VI. Plant Tests

Four series of body mixtures are given in Table I, and their expansion characteristics graphically demonstrate the possibilities of the use of expansion rings.

The test bodies were weighed in 10-kg. lots, thoroughly dry mixed, pugged, and tempered by hand. All bodies were aged overnight, wedged, and cut into bars to be fed into the auger. Twenty rings were extruded and eight rectangular bars with chamfered edges were hand pressed from each mixture.

Gloss, satin, and mat glazes were sprayed on four rings and two bars from each mixture. This left eight test rings of the original twenty, and two bars for future reference.

Preliminary tests proved that ring movement resulting from stress in the unglazed, unslipped body was fairly constant and of low magnitude. For this reason, only rings which had been sprayed with an underslip and glazed, as in actual terra-cotta production, were tested in these groups.

TABLE I

FOUR SERIES OF BODY MIXTURES FOR EXPANSION RINGS*

	Series A			
	X-1	X-2	X-3	X-4
Buff terra-cotta clay	50	47.5	45	42.5
Terra-cotta body grog (−12-mesh)	50	47.5	45	42.5
Red-firing, low-fusion clay		5	10	15
	100	100	100	100

	Series B			
	X-1	X-5	X-6	X-7
Buff terra-cotta clay	50	47.5	45	42.5
Terra-cotta body grog (−12-mesh)	50	47.5	45	42.5
Refractory sand clay (high in silica)		5	10	15
	100	100	100	100

	Series C				
	X-1	X-8	X-9	X-10	X-11
Buff terra-cotta clay	50	48.75	47.5	46.25	45
Terra-cotta body grog (−12-mesh)	50	48.75	47.5	46.25	45
Flint (−200-mesh)		2.5	5	7.5	10
	100	100	100	100	100

	Series D			
	X-12	X-13	X-14	X-15
Buff terra-cotta clay	48	48	48	48
Terra-cotta body grog (−12-mesh)	52	47	42	37
Sanitary-ware grog (−12-mesh)		5	10	15
	100	100	100	100

* Each mix contains 1½% of precipitated barium carbonate added.

VII. Results

Figures 5, 6, and 7 show the results of the tests. The amount of contraction in Fig. 5 is practically a linear function varying inversely with the concentration of red-firing clay. Curves (1), (2), and (3), respectively, represent rings sprayed with mat, satin, and gloss glazes. A relationship between the amount of crystalline growth and the actual coefficient of expansion is indicated in which the mat has the lowest thermal coefficient of expansion and the gloss the highest. That the matness is the result of crystalline growth is demonstrated by the fact that the mat glaze glosses on a rapid cooling schedule.

Calculated coefficients from Mayer and Havas data[8] show the following expansions:

Mat	Satin	Gloss
2.55×10^{-6}	2.37×10^{-6}	2.23×10^{-6}

[8] Max Mayer and Béla Havas, "Coefficient of Expansion of Enamels and Chemical Composition," *Sprechsaal*, **42** [34] 497–99 (1909); **44** [13] 188–90; [14] 207–209; [15] 220–22 (1911); tabular data are given on p. 40 of Enamels by A. I. Andrews. Twin City Printing Co., 1935. 428 pp. *Ceram. Abs.*, **14** [7] 158 (1935).

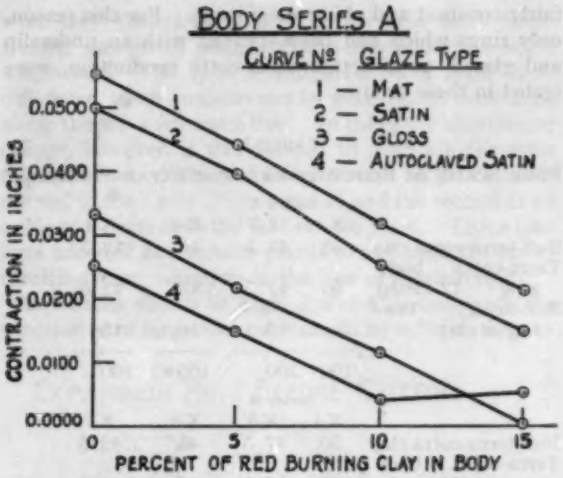

FIG. 5.—Test results; contraction is linear function varying inversely with clay concentration.

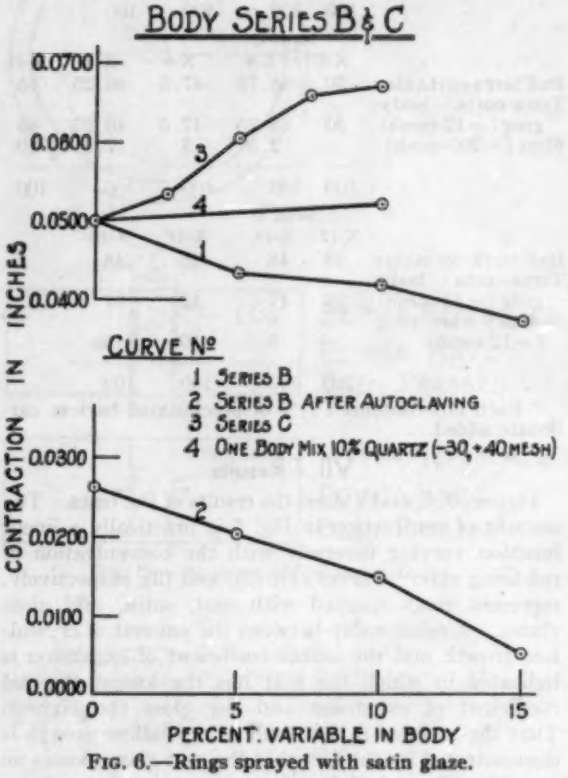

FIG. 6.—Rings sprayed with satin glaze.

This is a reversal of the expansion relationship demonstrated by the test rings. The Mayer and Havas data, however, which were calculated on a series run with any one type of glaze, gave fairly consistent indications of expansion characteristics.

Curve (4) in Fig. 5 was obtained by taking the difference in distances between the nibs before cutting and after cutting and autoclaving the rings sprayed with the satin glaze. The difference on the ordinate between curve (2) and curve (4) is a measure of the movement

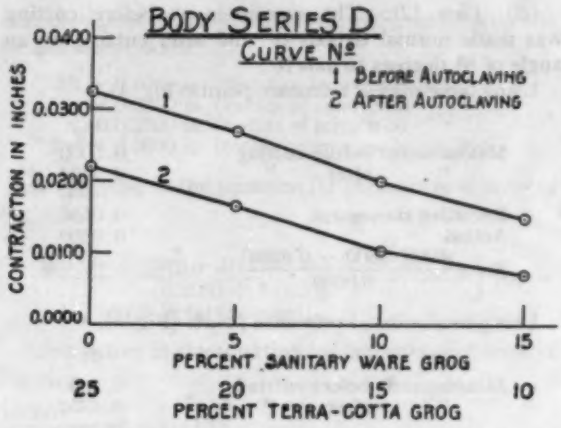

FIG. 7.—Effect of grog from sanitary ware vs. terra-cotta grog.

resulting from moisture expansion in the body. The tendency to craze from the kiln action proved practically a lineal function of the red-clay concentration, whereas the moisture expansion appeared to remain almost constant until 10% of the glassforming clay was reached; a definite lowering of the moisture expansion was then apparent. Some consideration in balancing a body must be given to the determination of the optimum amount of glassforming clay when lowering of the body thermal expansion (or the tendency toward kiln crazing) is partially offset by the reduction in moisture expansion. The algebraic sum of curve (2) and the moisture expansion gives curve (4), which represents the tendency to craze on weathering.

The test bars pressed from this series developed no shivering or crazing from the kiln. The autoclaved bars, however, that were sprayed with the gloss glaze, developed crazing, which ranged from slight at 0% of red clay to fine on those bars containing 15% of red clay. The autoclaved bars sprayed with satin and mat glazes produced no crazing.

Curve (1) Fig. 6, shows results on series B. Only the values for the rings sprayed with the satin glaze were plotted, inasmuch as the gloss and mat glazes had the same slopes as curve (1) and bore the same relationship as those of Fig. 5. This high-silica clay was used in the plant for setting terra cotta and sewer pipe because of its high fusion point. Inasmuch as this component was more of a sand than a clay, it was suspected of being high in free quartz and might therefore have been expected to produce shivering. Curve (1), however, showed an increase in concentration which produced a tendency toward crazing although to a far less extent than the red clay of series A. Autoclaving of the glazed rings of series B produced moisture expansion, which increased as the concentration became greater (see curve (2)). The use of this material in the body, therefore, not only increased the tendency toward kiln crazing but also toward weather crazing.

To determine the effect of silica as quartz, the content of −200-mesh flint was varied (see Fig. 6, series C). The flint caused such a contraction that it was difficult to cut the rings without breaking them (curve (3)). The

test bars with increasing flint content developed shivering on the chamfered edges. The autoclaved test bars of this series produced no crazing. An isolated mixture of 10% of Ottawa sand (through 30- on 40-mesh) was run to indicate the effect of larger grain size (curve (4)). Practically no registered effect was caused by the large quartz grains.

Figure 7, curve (1), demonstrates the effect of the substitution in the body mixture of grog made from sanitary ware for grog made from terra cotta. The autoclaved rings indicated that a slight reduction in moisture expansion might be expected with increasing sanitary-ware concentration. The reduced expansion probably was the result of the vitrified nature of the grog itself rather than any fluxing effect on the body.

Pieces of uncrushed sanitary ware, glazed with a terra-cotta gloss glaze, developed no crazing on autoclaving, whereas the same glaze crazed increasingly on the autoclaved terra-cotta test bars as the percentage of sanitary ware increased. The glaze and the sanitary ware apparently had practically the same thermal and moisture expansions so that a critical stress was not set up between them. Additions of the sanitary-ware grog to the terra-cotta body, however, lowered the body coefficient of thermal expansion so that there was less and less compressive stress in the glaze. Inasmuch as the sanitary-ware grog effected only a slight reduction in the moisture-expansion characteristics of the terra-cotta body, autoclaving caused enough moisture expansion to establish tension in the glaze.

All of the test bodies that showed glaze tension by the ring test developed crazing on the test bars.

VIII. Conclusions

The methods for testing expansion rings as outlined in the literature[5] have been reviewed, and about 600 die-extruded rings were measured. The following conclusions have been determined as a result of these tests: (1) Die extrusion of expansion rings makes possible the quantity production of rings and of such accuracy as to give reliable results; (2) when measurements are made with a micrometer caliper, the use of large nibs pressed in the body has inherent advantages over small reference points applied by hand; and (3) expansion rings afford an excellent means of registering the glaze and body stress relationships, and they may be used to predict accurately the degree of weather crazing caused by moisture expansion.

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POSSIBLE USE OF SUSPENDED ROOFS AND WALLS IN GLASS FURNACES*

By L. S. Longenecker

Abstract

Construction advantages and limitations of the sprung-type tank crown are discussed, and some modern heating chamber applications are shown in which the roof or crown has been changed in contour to secure better and more efficient heating. Developments have been made which indicate that a roof or crown may be used for more than just a top inclosure over a heating chamber. An explanation is given of how the present roof construction has been changed to secure these improved contour lines across and lengthwise of the heating chamber. Any of these features may be more generally applied to improved glass tank construction.

I. Introduction

In basic terms, a furnace or glass tank, to be an effective heating chamber, must be inclosed on all six sides. The material and construction must (1) be durable with one face exposed to high temperatures, (2) minimize heat losses, and (3) form proper contour lines for efficient heating. A discussion of the durability and insulation that result from the use of proper refractory materials will be omitted inasmuch as the design and construction of these inclosures is the subject of this paper.

The hearth or bottom steel (or pan) inclosure, generally so designed for efficiency in heating the glass, is paved with blocks or other suitable refractories, as well as a wall of blocks to one inch or so above the level of the molten material. The side and end walls above the block line are usually formed by stacking brick on brick and by bracing the stack with buckstays laterally arranged along the outside. The top or roof inclosure requires a more complicated structure. The sprung arch was no doubt the first method used to span this opening and to secure a roof inclosure.

II. Sprung Roof

The sprung roof or crown has proved to be structurally durable, particularly in glass tanks where silica brick may be used. Silica possesses good strength against crushing, practically up to its fusing point, which is a necessary requisite to withstand the heavy compression loads inherent in a relatively flat arch. The best clay brick, however, have a softening point considerably below their fusing point, and they may slowly yield to the stresses involved and eventually result in failure of the crown.

Although silica is stronger than clay under compression loads, it is also sensitive to sudden temperature changes, particularly below 1200°F. The glass plants again are fortunate because the operating conditions do not require temperature changes through this critical

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range, which would result in excessive thermal shock and spalling. Steel plants operate on a more or less intermittent schedule and cannot spare the time for slow heating and cooling. To secure a thermal-shock resisting material, clay brick and similar refractories are used in many furnace roofs. Silica, however, is used in the crown of the open-hearth furnace, which is operated continuously, and its life is determined by that of its roof.

III. Hung Roof

The hung roof design is generally used for high-temperature furnace roofs in the steel industry to overcome the structural weakness of clay refractories. In this type roof, all tile are supported by their top ends from a steel frame which spans the furnace. This method of roof construction, with the proper use of correctly spaced expansion joints, eliminates all compression loads on the tile, and there is also small tensile stress.

These hung, or suspended, clay roofs are therefore producing service results in excess of the best sprung roofs. The maintenance of these roofs is considerably easier because any local burned-out section may be repaired without the need of "scrapping" the entire roof. Their use, furthermore, has made it possible to increase the size of the furnace and to establish a greater factor of safety against any roof failure or collapse in the middle of a rush campaign.

The sprung arch or suspended roof will furnish about equal protection against heat loss and there will be no flame leakage if both are installed properly. A number of suspended clay arches are now partially insulated. The application of insulation on any type of refractory construction, however, will depend on the temperature and conditions inside the furnace. Insulation should be applied cautiously and increased or decreased in thickness as determined by the resulting service life of the refractories.

IV. The Arch

The arch, even though durable, is of such construction and contour that it is more or less only a roof inclosure. It has one set shape (see Fig. 1). It must always be higher in the center than at the skewback; the skewbacks and their supports must run fairly continuous along both sides of the roof, and they must be protected on the under face by a side wall or auxiliary arch. The thrust load, which must be well supported, requires closely spaced buckstays and adjustable tie rods. The working doors or firing ports through the side wall are therefore limited in size because they must be placed between the buckstays and under the skewbacks. In the case of the glass tank ports, the height of the port opening is determined by thermal requirements. This height, in turn, establishes the minimum height of the skewback. Apparently, this is the reason glass tank crowns are placed so high above the glass level.

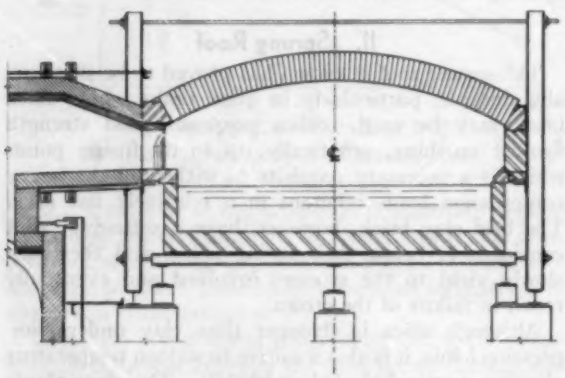

FIG. 1.—Cross section through conventional tank and sprung crown; *left*, section through conventional port; *right*, section through conventional breast wall.

V. Heating Chamber

A statement is often heard, "If you want to see how hot gases flow through and behave in a heating chamber, turn the chamber upside down, substitute water for the gas, and observe the behavior of the water." The roof and adjacent side walls are then the bottom which supports the water. The depth and width or the dimensions of any cross section through this stream of water are determined by the contour of the bottom. If this is a true analogy, then it must be admitted that, because of their buoyancy, the gases will rise and flow along the roof unless they are positively held down by means of a high port velocity and high furnace pressure adjacent the roof. A high velocity on the incoming ports means small ports, and small port openings on the regenerative furnaces are a decided "bottleneck" on the outgoing side.

Referring again to Fig. 1, the effectiveness of this heating chamber probably could be improved by using a flat roof in place of the upward curved roof. The excess space or inactive zone inclosed in the rise of the arch at least would then be eliminated. The roof could possibly be installed at a lower elevation, which would further reduce this inactive zone. Any reduction or elimination of this inactive zone should improve the effectiveness and control of heating.

With a flat roof surface located at the proper elevation, the depth of the combustion chamber and the thickness of the combustion space would be the same from side to side, and the complete heating chamber volume would be active and alive. The spaces adjacent the side walls of a heating chamber require the most heat owing to the conduction losses through these walls. In an arched chamber, however, the depth of the combustion space is less in this region of greatest heat demand. These items of heating-chamber uniformity apparently are important in a steel-plant reheating furnace, and a flat roof across the furnace is necessary in order to heat the slabs evenly from end to end. The alternating method of firing across the glass tank may help to even off any nonuniformity of heating. The molten condition of the glass also allows it to circulate by convection, which may eliminate harmful hot and cold spots. It must be admitted, however, that a type of heating is preferable which results in a uniform high top temperature throughout.

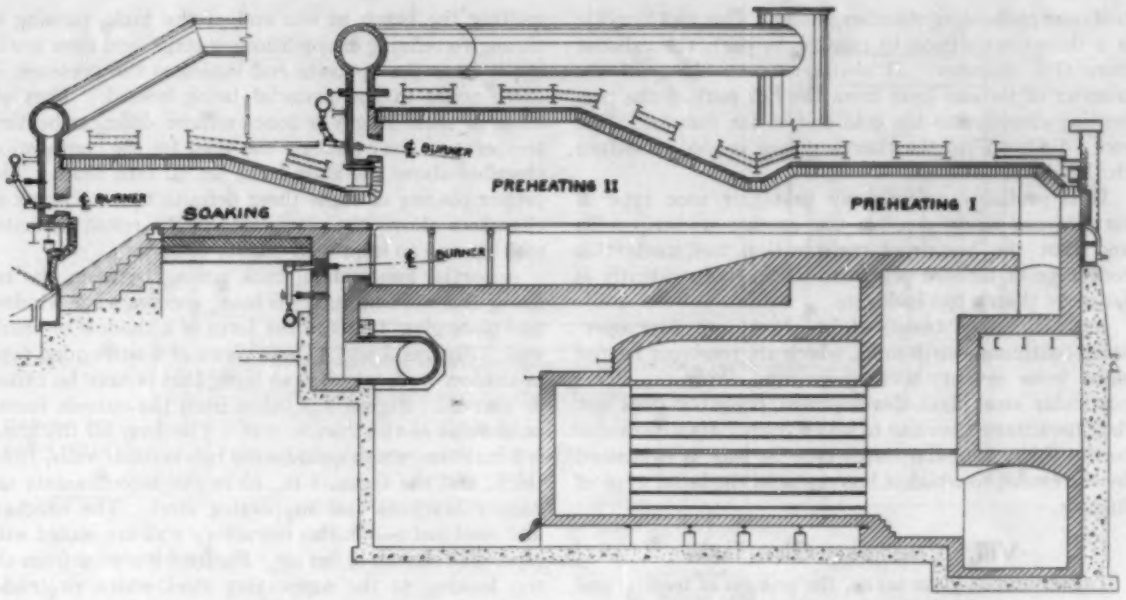

FIG. 2.—Longitudinal section through a continuous-type, triple-fired, slab reheating furnace.

VI. Slab Heating Furnace

Figure 2 is a longitudinal section through what is known in the steel industry as a continuous, triple-fired, slab reheating furnace. The end burners in the wall on the left side directly over the discharge door heat and control the "soaking" chamber. The second burner wall, located midway the furnace length, heats and controls the top part of the "preheating" chambers, and the burners, which are directly below and under the skid rails, supply heat to the bottom side of the slabs.

The slabs are pushed through the furnace edge to edge, and when one is entered at the charging end, a heated slab is pushed off the hearth and discharged at the opposite end. From the entering end to the middle burner wall, the slabs ride on spaced piers, top faced with water-cooled pipes, which allow suitable space for bottom firing. At the midburner wall, the slabs pass on to a refractory hearth, which eliminates black streaks that may result from the use of water-cooled skids. The solid hearth or soaking chamber is not bottom fired.

This zone-type furnace is reputed to heat rapidly with no sacrifice in quality of heating throughout a variable range of production. It is generally stated that steel is not damaged by fast heating but by overheating. If steel is subjected to too hot a flame, when the temperature approaches 2200°F., its surface will melt or "wash," which in steel terminology is overheating.

A high temperature or thermal head is required of the flame to secure rapid or forced heating, but this high temperature may be used with safety only when the steel batch is well below 2200°F. The heating chamber above the hearth level therefore has been zoned, and the fuel is applied according to the heat-absorbing requirement of the product.

The slabs are cold, or nearly so, when they enter this furnace, and as they pass through the No. I preheating chamber, they absorb heat from the products of combustion. This pulls the high preheating temperature down to a point where the exhaust gases may be safely handled by the recuperator. As the slabs approach and enter the next preheating chamber, No. II, they come under the direct influence of the highest thermal head in the furnace. The firing rate of this chamber is controlled so that the slabs pass under the middle burner wall, and they leave this preheating chamber with a surface temperature around 2200°F. On full load, the roof thermocouples in preheating chamber No. II read approximately 2750°F., which is about the top firing rate.

VII. Soaking Chamber

In the soaking chamber, the roof thermocouples read approximately 2300°F., and they are held closely within a narrow range only 50° to 80° above the proper rolling temperature. It has been found through experience that any higher temperature in this soaking zone will either "wash" the slabs or cause a sticky and objectionable scale condition.

The main object of this soaking chamber, apparently, is to permit the inside of the slabs to reach a temperature nearly equal that of the surface.

The suspended nose and burner wall effectively separates the chambers and permits each chamber to be fired separately. This dipped-down roof knuckle also blocks off all radiant heat from one chamber to the other. The high temperature in the preheating chamber, therefore, cannot affect the lower temperature in the soaking chamber. The products of combustion from the soaking chamber exhaust into the preheating zone and then out the bottom ducts next to the charging end.

There is also a roof knuckle at the end of the sloping

roof over preheating chamber No. II. This roof knuckle is a throat restriction to control, in part, the exhaust from this chamber. It also serves to block off the transfer of radiant heat from the hot part of the preheating chamber to the cold end of the furnace. The roof "dipdown" at the charging door is used to reduce the height of the door.

It is probably safe to say that this zone type of furnace has made possible the continuous strip mills and that the hung-roof construction has made this zone type of furnace practical. This roof evidently is far more than a top inclosure.

Approximately twenty-eight plants are now operating continuous strip mills, which are receiving heated slabs from seventy-seven zone-fired furnaces. This particular steel-plant development probably does not date back more than five to seven years. Its superiority to the old rectangular batch-type furnace is evidenced by the extent to which it has replaced the latter type of furnace.

VIII. Continuous Glass Tanks

In continuous glass tanks, the process of feeding and melting the batch at one end of the tank, passing it through a refining or conditioning stage, and then working it from the opposite end indicates the presence of three zones in the material being heated. That all three of these stages or zones require different heating temperature may indicate the need for the combustion chamber above the glass to be set off into zones. The proper placing of these three definite heating zones or chambers above the glass level might result in faster melting and an improved quality of glass.

A partial longitudinal tank zoning between the refining and working stages is being used on some window and plate glass tanks in the form of a shadow or shade wall. Figures 3 and 4 show views of a suspended type of shadow wall, which is so hung that it may be raised or lowered. Figure 3 is taken from the outside facing at the end of the shadow wall. The over-all thickness is 3 ft., 10 in., which includes the two vertical walls, 12 in. thick, and the space, 1 ft., 10 in., to accommodate the hanger brackets and supporting steel. The brackets and steel inclosed in this refractory wall are cooled with a positive stream of fan air. Figure 4 is a view from the top looking at the supporting steel which protrudes

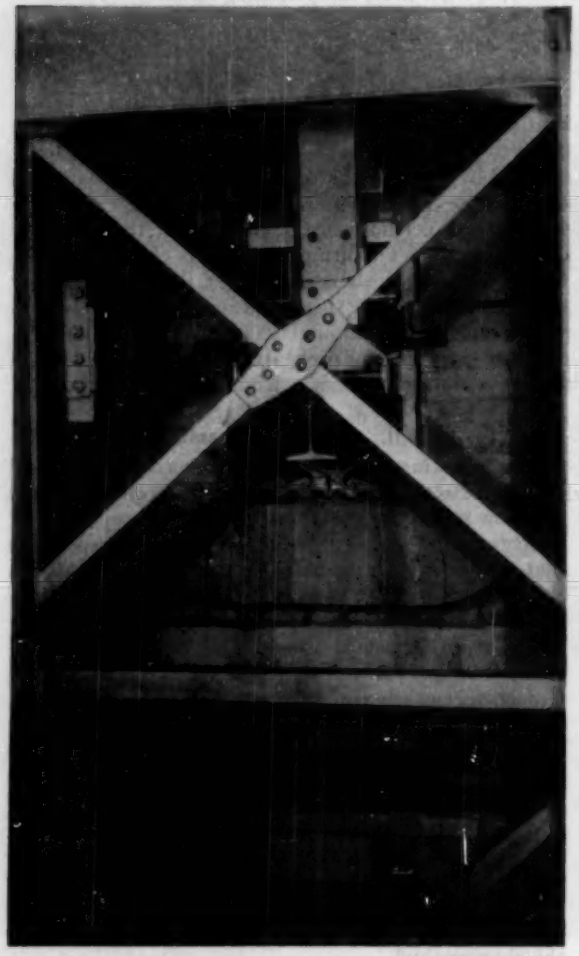

FIG. 3.—Outside facing of suspended type shadow wall.

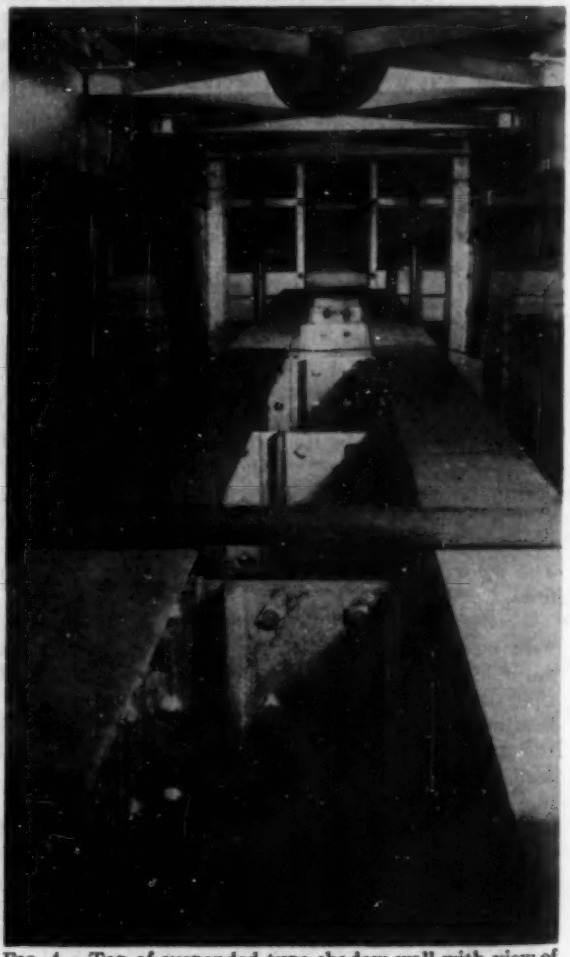

FIG. 4.—Top of suspended type shadow wall with view of supporting steel protruding above.

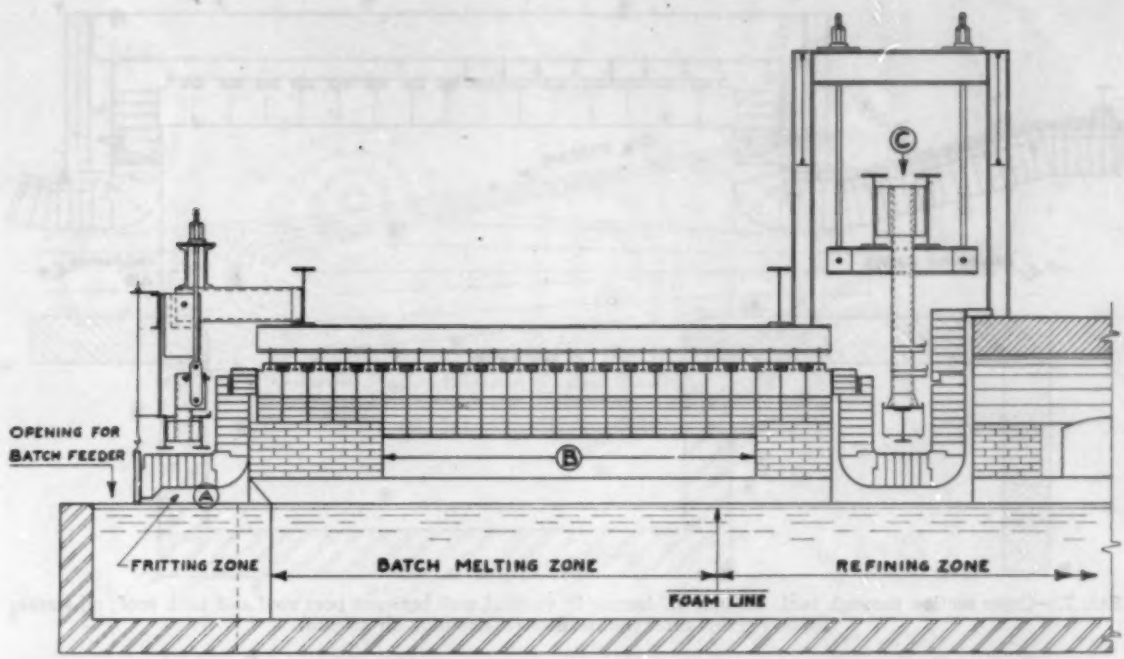

FIG. 5.—Longitudinal section through melting end of glass tank equipped with suspended back wall, crown, and shadow wall; *A*, fritting chamber under back wall; *B*, continuous long port; and *C*, adjustable shadow wall between melting and refining chambers.

above the shadow wall. These beams are so framed that the entire shadow wall is suspended from an overhead bridge by four hanger bolts. This adjustable feature, combined with the flat contour from end to end, furnishes a definite control or separation between chambers.

These shadow walls are usually located in the vicinity of the floaters and are considered to be located between the refining and working zone. This refractory damper not only serves to control the amount of flame travel between chambers, but it also serves as a baffle which blocks off radiant-heat transfer. In view of the fact that glassmelting is really accomplished in three zones, it appears logical that a similar shadow wall could profitably be used between the melting and refining zones. Figure 5 shows a longitudinal section through the melting end of a tank that is equipped with a suspended shadow wall between the melting and refining zones. The tank also has a suspended back wall, a suspended crown, and a suspended port roof. The various zones are designated as fritting, batch melting, and refining. The working zone beyond the refining zone is not shown.

The low roof section on the lower part of the back wall forms the fritting chamber, marked *A*. This is the anteroom through which the newly fed batch passes and in which its top surface is fused into a glazed mass. This glazed surface seals in the dry batch and thereby reduces dusting or dust pickup by the high velocity flame in the melting chamber. The roof over chamber *A* is sufficiently low so that flame or gas travel is almost entirely prevented. The one open side to the tank allows enough radiant heat to enter to accomplish a good degree of glazing.

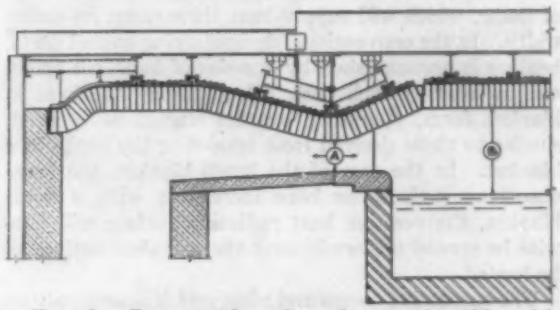

FIG. 6.—Cross section through port knuckle with suspended roof over port and tank; height and location of port opening, *A*, is independent of roof height, *B*, and vice versa.

The chamber from the back wall to the shadow wall incloses the batch melting zone, foam line, and beginning of the refining process. Its over-all length is such that it will include all surfaces that will benefit by a high thermal differential.

On the opposite side of the shadow wall, *C*, is shown the main refining chamber. This chamber, positively separated from the melting end, may be suitably fired and controlled to establish a uniform glass temperature, comparable to the soaking zone of the steel-heating furnace.

The shadow wall, *C*, is adjustably suspended so that it may be raised or lowered to permit some control of the throat opening between the chambers. This throat will partly control the amount of gas travel between chambers, and the shadow wall itself will block off radiant heat transfer.

The melting zone is heated by one continuous long

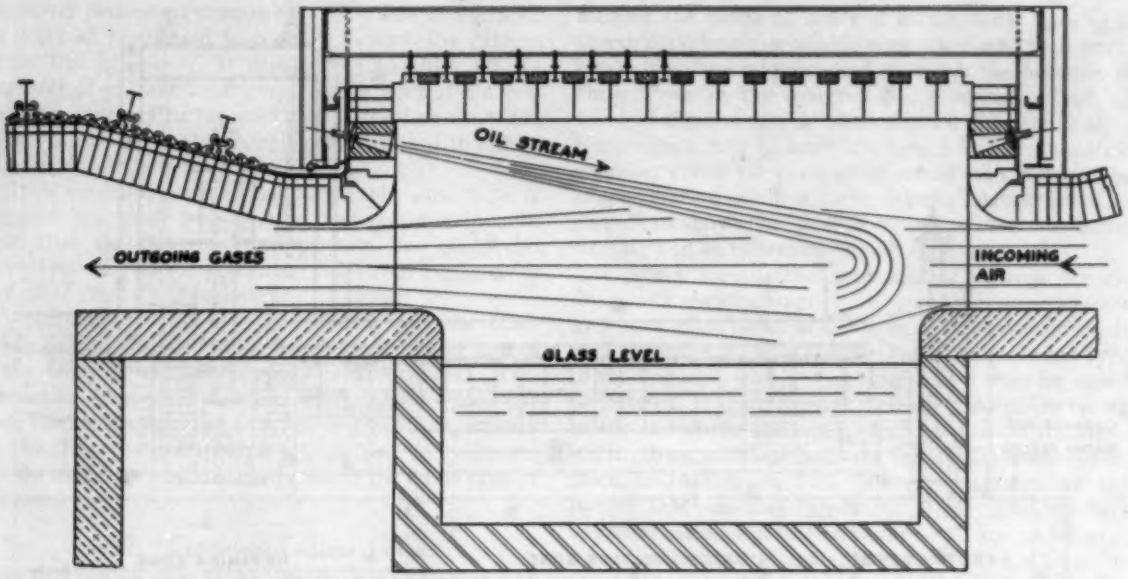

FIG. 7.—Cross section through tank showing oil burner in vertical wall between port roof and tank roof; oil stream applied across tank counterflow to incoming air stream.

port, marked *B*. This width of port is easily obtained when a hung roof is used which extends over the tank and the port. One wide port provides a blanket-type of flame, which will supply heat throughout its entire width. In the conventional design having spaced ports, heating is accomplished by a series of local hot spots, one in front of each port. By applying the heat in blanket form, operating benefits should be secured, similar to those derived from spreading the batch in a blanket. In the case of the batch blanket, the heat-absorbing surface has been increased; with a flame blanket, the positive heat radiating surface will likewise be spread uniformly over the complete surface to be heated.

The suspended crown and wide port is shown only on the melting zone in which most of the heavy firing is done. In this zone, it is apparently important to secure what may be termed forced heating to melt the batch quickly. The lower suspended roof and inclosing shadow wall should make it easier to control and to establish a more effective melting condition without upsetting any balance which may be required in the refining zone.

The roof over the refining zone may be of the conventional arch type, inasmuch as the heat requirement in this zone is what may be termed space heating. The amount of fuel burned in this chamber obviously need not be so great.

Figure 6 is a cross section through the port and crown of the tank shown in Fig. 5. The port opening appears shallow. Its area, however, is equal to that of the individual ports of a conventional tank which it would replace. The roof contour over the uptake ducts and port are shaped to produce proper streamlining. The port knuckle joins into the suspended flat crown so that the elevation of either may be changed without affecting the elevation of the other. The port knuckle may also be placed a greater distance back in the port, moved toward the tank, or even placed in the tank beyond the port floor. These designs show that a hung roof permits considerable construction flexibility and improvements that were previously impossible when an arched crown was used.

IX. Oil-Burning Glass Tank

Figure 7 is a proposed design of glass tank for burning oil. It is equipped with a hung roof and so designed that the oil burners may be placed in the vertical wall above the port. The oil burners can then be placed so that the stream of atomized oil is directed across the tank and into the air stream, which is coming in from the opposite side.

An oil stream thus applied may require coarser atomization, but because it passes over the top of the combustion blanket, any oil droplets that are not properly atomized will burn while falling through this blanket before hitting the glass surface. The travel distance across the tank from the nozzle to the incoming air stream allows sufficient distance to use up the kinetic energy of the high nozzle velocity. The unburned portion would be picked up by the incoming air stream and carried back across the tank. This double travel across the tank should result in good combustion and in the elimination of hot spots.

X. Conclusion

The hung roof, which requires special shaped tile, tile hangers, and a supporting steel frame, will naturally cost more for the initial installation than a conventional crown. Inasmuch as the hung roof serves the double purpose of a roof inclosure and a means of heat control, its added cost may be justified.

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